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# Di-calcium phosphate by direct acidulation of phosphate rock

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# DI-CALCIUM PHOSPHATE BY DIRECT ACIDULATION OF PHOSPHATE ROCK

by

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## ABSTRACT

An investigation was undertaken to develop a process for producing di-calcium phosphate by direct acidulation of phosphate rock. In general, when phosphate rock is treated with sulfuric acid, mono-calcium phosphate or phosphoric acid is formed.

If less sulfuric acid is used, di-calcium phosphate should be formed theoretically, however only mono-calcium phosphate and undecomposed phosphate rock result in practice.

Both mono-calcium phosphate and di-calcium phosphate are effective plant foods, however di-calcium phosphate not only requires less sulfuric acid in manufacture but is also neutral and has good physical properties. As both temperature and concentration have an important effect on the formation of di-calcium phosphate, knowledge of the equilibria in the system $CaO-P_2O_5-SO_3-H_2O$ was required. This was determined in the laboratory at 100°C. and 145°C. Equilibria in the ternary system $CaO-SO_3-H_2O$ was also investigated at 100°C. and 145°C. as well as in the ternary system $CaO-P_2O_5-H_2O$ at 145°C.

The $CaO-P_2O_5-SO_3-H_2O$ system is a four component system and a graphical representation proved rather difficult. However, for that part of the quaternary system which was of interest, a graphical method of representation was developed in two dimensions.

By using the phase relationships, a cyclic process for the manufacture of di-calcium phosphate was proposed.

This process consists of precipitating calcium with sulfuric acid, separating calcium sulfate, forming di-calcium phosphate by adding

phosphate rock to the filtrate and final separation of di-calcium phosphates.

In laboratory scale work the optimum conditions were studied. A final acidulation mol ratio of 2.16 gave a maximum citrate soluble $P_2O_5$ content of 33.8 percent, equivalent to 94 percent $P_2O_5$ availability. In general high temperature curing had little effect on the $P_2O_5$ availability. The maximum product contained 94.6 percent $P_2O_5$ availability, 41.4 percent total $P_2O_5$, 33.8 percent citrate soluble $P_2O_5$ and 5.4 percent water soluble $P_2O_5$.

Pilot plant tests were made to demonstrate the process on a continuous basis. In the pilot plant calcium sulfate was separated by settling and di-calcium phosphate was not separated. Additional phosphate rock was added to the solution to form a solid product which was converted in paddle conveyers. The resulting acidulation ratio was 1.58 by weight instead of the 2.16 used in the laboratory.

Di-calcium phosphate was obtained in the pilot plant by this method without cyclic mixing or filtration. A product averaging 40 percent total $P_2O_5$, 33.2 percent citrate soluble $P_2O_5$ and 92 percent $P_2O_5$ availability was obtained.

A preliminary cost estimation indicated the proposed di-calcium phosphate process was favored.

# INTRODUCTION

Most of the phosphate fertilizer used throughout the world is supplied in the form of superphosphate, manufactured by acidulating phosphate rock with sulfuric acid or phosphoric acid. The acidulation process converts the highly insoluble phosphate in mineral apatite into forms which are available to plants, such as mono-calcium phosphate $Ca(H_2PO_4)_2$ and di-calcium phosphate $CaHPO_4$.

When phosphate rock is treated with sufficient acid, mono-calcium phosphate or phosphoric acid can be formed. If less sulfuric acid is used di-calcium phosphate should be formed theoretically, however only mono-calcium phosphate and undecomposed phosphate rock result in practice. Acidulation to di-calcium phosphate is of considerable interest since less sulfuric acid would be required, thereby lowering production costs.

In addition, di-calcium phosphate has many desirable properties as a source of plant food. It is also neutral and has good physical properties (52). Di-calcium phosphate can be produced by neutralizing phosphoric acid with limestone or ammonia, but this process is of little interest since the cost of production is relatively high.

Phosphate rock consists of the mineral apatite, usually fluorapatite $Ca_{10}F_2(PO_4)_6$, plus impurities. When sulfuric acid is added it not only reacts with the apatite but also with the calcium fluoride in the apatite structure, and directly or indirectly with such impurities as organic matter, iron and aluminum compounds, carbonates of lime and magnesium (24).

During acidulation, the apatite structure is destroyed. For

convenience this action may be represented by a series of reactions between sulfuric acid, tri-calcium phosphate and calcium fluoride. The tri-calcium phosphate is converted into a mixture of calcium sulfate and mono-calcium phosphate mono-hydrate. The calcium fluoride is partially converted to hydrofluoric acid. Mono-calcium phosphate and calcium sulfate are the chief constituents of ordinary superphosphate. The overall reaction may be represented as follows:

$$Ca_{10}F_2(PO_4)_6 + 6\ H_2SO_4 + 3\ H_2O = 3\ Ca(H_2PO_4)_2 \cdot H_2O + 6\ CaSO_4 + CaF_2 \qquad (1)$$

If less sulfuric acid is used than that required by the above reaction, the following reaction is possible:

$$Ca_{10}F_2(PO_4)_6 + 3\ H_2SO_4 = 6\ CaHPO_4 + 3\ CaSO_4 + CaF_2 \qquad (2)$$

However, when this reaction is attempted a mixture of mono-calcium phosphate and undecomposed phosphate rock is obtained instead of di-calcium phosphate. The purpose of this research was to find a method of producing di-calcium phosphate.

Reaction 2 is very difficult to effect. Phosphate rock so treated always contains a high percentage of undecomposed rock, even after a relatively long time. Failure to produce di-calcium phosphate by this acidulation suggested that knowledge of the decomposition of rock phosphate with sulfuric acid at various temperatures was needed. To provide this, the equilibria in the system $CaO-P_2O_5-SO_3-H_2O$ was developed since existing information regarding the actual or assumed states of equilibrium in this system was insufficient.

Since the $CaO-P_2O_5-SO_3-H_2O$ system is a four component system, a

graphical representation proved rather difficult. However, for that part of the quaternary system which is of interest, a two dimensional, four component graphical method was developed. Experimental data were used where literature data were inadequate or nonexistent.

As a result of these studies a cyclic process to produce dicalcium phosphate by direct acidulation of phosphate rock is proposed and has been demonstrated on a pilot plant scale.

# REVIEW OF THE LITERATURE

## Phase Equilibria

### Ternary system $CaO-SO_3-H_2O$

Hulett, Allen and Euler (31) determined the solubility of $CaSO_4 \cdot 2H_2O$ in water. Chasseveut (14) studied the solubility of unstable calcium sulfate hemihydrate in water. Straub, Partridge and White (31) determined the solubility of calcium sulfate in water at temperature above 100°C. Cameron (31) investigated the solubility of calcium sulfate in sulfuric acid solution at 25°C., 35°C. and 43°C.

### Ternary system $CaO-P_2O_5-H_2O$

Bassett and Clark (3, 15), and Cameron and Seidell (12) investigated the system of $CaO-P_2O_5-H_2O$ at 20°C., 40°C., and 50.7°C. Bassett (3) obtained some data above 100°C. Belopolski, Taparova, Sserebrennikova and Shulgina (4, 5, 6) also investigated the ternary system of $CaO-P_2O_5-H_2O$. They give a phase diagram at 80°C. for $P_2O_5$ concentrations of 0.13-48.9 percent. Elmore and Farr (23) and Frear and Elmore (18) studied the equilibrium in the system $CaO-P_2O_5-H_2O$ in 2-98 percent $H_3PO_4$ at 25°C., 40°C., 75°C. and 100°C. They found that di-calcium phosphate is stable in equilibrium with 2-27 percent $H_3PO_4$ at 25°C. and in 2-53 percent acid at 100°C. They also found that mono-calcium phosphate mono-hydrate is in equilibrium with 18-86 percent $H_3PO_4$ at 25°C. and with 48-76 percent $H_3PO_4$ at 25°C. and with 48-76 percent $H_3PO_4$ at 100°C. Mono-calcium phosphate was shown to be a saturated solid in 86-98 percent $H_3PO_4$.

Quaternary system $CaO-P_2O_5-SO_3-H_2O$

Taber (50) determined the solubility of calcium sulfate in aqueous solutions of phosphoric acid at 25°C. Hofer (30) studied the system at 25°C. and 83°C. Cameron (30) investigated the system at temperatures of 25°C. and 66°C. He concluded that the solid gypsum becomes unstable above a temperature of 66°C. Increasing temperature increases the range of di-calcium phosphate and anhydrous calcium sulfate.

Sanfourche (44) determined the solubility of calcium sulfate in phosphoric acid solution at temperatures from 15°C. to 110°C. However they did not give densities of the solutions or explain how they converted the results into the terms of volumes given in their table. The values calculated from the sulfate are higher than those calculated from the calcium.

Campbell and Courts (13) studied the $CaO-P_2O_5-SO_3-H_2O$ system at 73.3°C. They claimed that the solubility relationship in the system changes very slightly upon the addition of $SO_3$. As the concentration of $P_2O_5$ increases, the solubility of $CaSO_4$ in the solution becomes negligibly small.

Belopolski, Sserebrennikova and Taparova (6, 51) determined the solubility of calcium sulfate in phosphoric acid solution at 0-63 percent concentrations of $H_3PO_4$ at 25°C., 40°C., 60°C. and 80°C. The only stable solid phase observed at 80°C. was $CaSO_4$. The solubility curves of $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot \frac{1}{2}H_2O$ intersected each other at $P_2O_5$ concentration of 33 percent. The dihydrate is more stable below this concentration and hemihydrate is more stable above this concentration.

## Processes for Di-Calcium Phosphate

Commercial feed grade di-calcium phosphate is prepared by reacting phosphoric acid with high grade limestone or burnt lime. The basic process was developed by the Tennessee Valley Authority (35, 41) and has been modified by several investigators (17, 28, 29, 42, 45, 46, 54).

In this process, phosphoric acid, high grade limestone and water are stirred together vigorously in a mixing chamber. The solution pH is controlled to form di-calcium phosphate of 98 percent purity. No saving of sulfuric acid is obtained, however, as can be seen by representing the reaction as follows:

$$Ca_{10}F_2(PO_4)_6 + 9\ H_2SO_4 = 6\ H_3PO_4 + 9\ CaSO_4 + CaF_2 \qquad (3)$$

$$H_3PO_4 + CaCO_3 = CaHPO_4 + 2\ H_2O + 2\ CO_2 \qquad (4)$$

Three moles of sulfuric acid are required per mole of $P_2O_5$ in this solution. Direct acidulation requires only one mole of sulfuric acid.

The $H_3PO_4$ in the second reaction 4 may be obtained from the electric furnace process. However, such acid is generally too expensive to use in fertilizer manufacture.

Several development processes have been reported which are not in commercial use. Patal (38) treated phosphate rock with a mixture of sulfuric acid and hydrochloric acid of sufficient proportions to form mono-calcium phosphate. The calcium sulfate and insoluble residue from the acid solution were separated by filtration. The filtrate was evaporated to dryness and the dried product heated sufficiently to drive off the hydrochloric acid and convert the soluble salt into

di-calcium phosphate. The hydrochloric acid was collected to be reused.

Fox and Clark (21) proposed a process somewhat similar to Memminger (32). Newberry and Barret (34) consisting of first producing calcium mono-chlorophosphate $CaClH_2PO_4.H_2O$, then decomposing this compound with steam at a temperature of 200°C. to 400°C. according to the following equation:

$$CaClH_2PO_4.H_2O + \text{steam} = CaHPO_4 + HCl + H_2O \qquad (5)$$

Pike (39), and Seyfried (48, 49) proposed a process in which HCl gas is passed through a column of unground phosphate rock over which water is sprayed. In this process phosphoric acid, mono-calcium phosphate and calcium chloride are continually withdrawn from the base of the tower as fresh rock is fed into the top. The acid solution then is partially neutralized with lime in a separate chamber to produce di-calcium phosphate. In actual practice, however, these methods have objectionable practical features.

Two processes were studied by the Tennessee Valley Authority involving the acidulation of phosphate rock with phosphoric acid, using less acid than normally required for superphosphate (55). The first, a pressure process, was patented by Zbornik (56). The phosphoric acid and phosphate rock were mixed in an autoclave under a pressure of more than 25 psi. A product in which 95 percent of the $P_2O_5$ was available[1] was obtained using an acidulation ratio of about 1.0. Feng (20) recently

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[1] $P_2O_5$ availability $= \dfrac{\text{Total } P_2O_5 - \text{Citrate insoluble } P_2O_5}{\text{Total } P_2O_5} \times 100$

investigated this process but could obtain only about 92 percent conversion.

The second process of the Tennessee Valley Authority (2, 19) was a cyclic process, involving the hydrolysis of triple superphosphate. The superphosphate was hydrolyzed to form di-calcium phosphate and an aqueous solution of phosphoric acid and mono-calcium phosphate. The di-calcium phosphate was filtered off and dried. The filtrate was combined with phosphoric acid used in the preparation of superphosphate.

Hughes and Cameron (25) proposed a process for producing di-calcium phosphate by using sulfur dioxide and sulfurous acid at 25°C. to 100°C. and a pressure from 3 to 10 atmospheres. Curtis (16) proposed a three step process for the manufacture of di-calcium phosphate from bone and sulfur dioxide. Bergmann (7), Scadtler (47) and Thilo (53) also proposed processes using sulfur dioxide or chlorine gases or both to treat an aqueous solution of ground phosphate rock to produce di-calcium phosphate. Frear and Knox (22, 27) proposed a process in which molten rock phosphate was quenched in dilute phosphoric acid. None of these methods are commercially important.

Other cyclic processes are somewhat similar to the Tennessee Valley Authority method. Bridger, Horzella and Lin (9) studied a process in which phosphate rock was reacted with mono-calcium phosphate, triplesuperphosphate or mineral acid to produce di-calcium phosphate. The process consisted of hydrolyzing a mixture of phosphate rock, mono-calcium phosphate monohydrate, superphosphate or acids, followed by heating in an open container at 185°C. These steps were repeated at least three times. When triplesuperphosphate or phosphoric acid was

used, the acidulation required to produce the fertilizer was only 50 percent of that required for the production of ordinary triplesuperphosphate. When sulfuric acid or normal superphosphate was used, higher acidulations were required.

Kaufman (26) studied this process on a pilot plant scale. He showed a $P_2O_5$ availability increase from an equivalent 82.4 percent in the feed to 88.2 percent in the product.

## MECHANISM OF ACIDULATION OF PHOSPHATE ROCK

If the acidulation of phosphate rock is considered as a heterogeneous solid-liquid reaction, diffusion phenomenon may be considered as having an important influence in the acidulation process. The acidulation process can be visualized as a chemical reaction at surface of the rock followed by diffusion of acid ions and products. The chemical reaction may be represented as:

$$Ca_{10}F_2(PO_4)_6 + 6H^+ \rightleftharpoons 6HPO_4^{=} + 9Ca^{++} + CaF_2 \qquad (6)$$

$$Ca_{10}F_2(PO_4)_6 + 12H^+ \rightleftharpoons 6H_2PO_4^- + 9Ca^{++} + CaF_2 \qquad (7)$$

Because of concentration differences, ions from the resulting solution diffuse through the boundary layer to the solid surface and the products of reaction diffuse through the boundary layer to the solution.

The amount of phosphate rock which is dissolved per unit of time is known to be dependent on the speed and time of stirring. Therefore, it can be assumed that the rate of dissolution at the boundary surface of the phosphate rock is probably many times greater than the rate of diffusion. In a sequence of a slow and a very fast process, the slow process controls the rate. We can conclude that the acidulation process is controlled by the rate of diffusion, with rapid establishment of ion equilibrium.

The $HPO_4^{=}$ ions resulting from reaction 6 will immediately react as follows:

$$HPO_4^{=} + H^+ \rightleftharpoons H_2PO_4^- \qquad (8)$$

$$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4 \qquad (9)$$

Actually, the acidulation of phosphate rock results in $Ca^{++}$ ions, un-ionized $H_3PO_4$, $SO_4^=$, $H_2PO_4^-$ and $HPO_4^=$ ions. The existing ions and molecules are in mutual equilibrium and may be assumed to diffuse from the boundary of the surface to the solution at a velocity approximately the same as the $H^+$ ions diffuse from the solution to the boundary layer. The diffusion velocity determines the rate of acidulation of phosphate rock. The mechanism of the main chemical reaction can be characterized by the total equation.

$$mCa_3(PO_4)_2 + 2nH^+ + nSO_4^= \rightleftharpoons 3mCa^{++} + aH_3PO_4 + bH_2PO_4^- + cHPO_4^= + dH^+ + nSO_4 \qquad (10)$$

m = the number of mols of tri-calcium phosphate dissolved at a given moment per volume of solution.

n = the number of mols of sulfuric acid available at the beginning of the dissolving process per volume of solution.

a, b, c, d = the number of ions or molecules in the solution at a given moment per volume of solution.

If the volume of solution is represented by v, the reaction equilibrium may be represented by:

$$aH_3PO_4 \rightleftharpoons dH^+ + bH_2PO_4^- \qquad (11)$$

$$b \cdot d = K_1 a \cdot v$$

where $K_1 = 7.54 \times 10^{-3}$ mol/c.c (36)

$$b H_2PO_4^- \rightleftharpoons c HPO_4^{=} + d H^+ \qquad (12)$$

$$d \cdot c = K_2 \cdot b \cdot v$$

where $K_2 = 6.23 \times 10^{-8}$ mol/c.c. (37) and

where $K_1$ and $K_2$ are the first and second ionization constant of phosphoric acid and $3a + 2b + c + d = 2n$ (H balance), also $a + b + c = 2m$ (P balance).

As the process continues and the $C_{H^+}$ of the solution decreases, the $C_{HPO_4^{=}}$ and $C_{Ca^{++}}$ of the boundary layer will increase. Eventually the precipitation of di-calcium phosphate and calcium sulfate will begin according to the following reaction:

$$CaSO_4 \rightleftharpoons Ca^{++} + SO_4^{=} \qquad (13)$$

$$K_{sp} = C_{Ca^{++}} \cdot C_{SO_4^{=}}$$

where $K_{sp} = 2.16 \times 10^{-4}$

$$CaHPO_4 \rightleftharpoons Ca^{++} + HPO_4^{=} \qquad (14)$$

$$K_{sp} = C_{Ca^{++}} \cdot C_{HPO_4^{=}}$$

where $K_{sp} = 3.04 \times 10^{-5}$

Since the value of the solubility product constants are very small, equilibrium is quickly established for di-calcium phosphate and calcium sulfate, and any unreacted phosphate rock is almost immediately covered with a layer of solid deposits of di-calcium phosphate or calcium sulfate. Removal of these solid products is therefore necessary for further conversion.

Besides the main component apatite, phosphate rock also contains calcium fluoride, iron, aluminum, magnesium, and calcium carbonate. Many side reactions will occur during the acidulation process.

Calcium fluoride is found in phosphate rock in the free state or combined with tri-calcium phosphate in the apatite molecule $Ca_{10}F_2(PO_4)_6$. It reacts with sulfuric acid as follows:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF \qquad (15)$$

The hydrofluoric acid (HF) subsequently reacts with the silica present in the rock to form $SiF_4$ according to the following reaction:

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \qquad (16)$$

The silicon tetrafluoride is then decomposed by water to form silica and hydrofluosilicic acid as follows:

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6 \qquad (17)$$

The reaction between sulfuric acid and iron contained in phosphate rock is not known, since the iron is probably distributed between the sulfate and phosphate. The reaction may be represented as follows:

$$2FePO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_3PO_4 \qquad (18)$$

This reaction is more or less reversible and in the presence of water, hydrated iron phosphate is formed:

$$Fe_2(SO_4)_3 + 2H_3PO_4 + 4H_2O \longrightarrow 2FePO_4 \cdot 2H_2O + 3H_2SO_4 \qquad (19)$$

Hydrated iron phosphate may be converted into the less soluble anhydrous form by reacting with anhydrous calcium sulfate, the latter compound being converted into gypsum as:

$$FePO_4 \cdot 2H_2O + CaSO_4 \longrightarrow CaSO_4 \cdot 2H_2O + FePO_4 \qquad (20)$$

The reaction between sulfuric acid and aluminum in phosphate rock is similar to that of iron.

Sulfuric acid acts upon calcium or magnesium carbonate to form magnesium sulfate or calcium sulfate, water, and carbon dioxide in accordance with the following reactions:

$$H_2SO_4 + MgCO_3 \longrightarrow MgSO_4 + CO_2 + H_2O \qquad (21)$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + CO_2 + H_2O \qquad (22)$$

# STUDY OF THE QUATERNARY SYSTEM $CaO-P_2O_5-SO_3-H_2O$ AT DIFFERENT TEMPERATURES

The phase relationships of the quaternary system $CaO-P_2O_5-SO_3-H_2O$ at 25°C. have been determined by Cameron (30) and Taber (50) at 83°C. by Hofer (30) and from 15°C. to 110°C. by Sanfourche (44). The phase relationships of the ternary system $CaO-P_2O_5-H_2O$ at 100°C. has been investigated by Elmore and Farr (23). Straub, Partridge and White (31) have determined the solubility of calcium sulfate in water at temperatures above 100°C. They analyzed only a relatively few samples and data is insufficient for adequate description of the di-calcium phosphate process.

To supplement the data available from the literature for the quaternary system $CaO-P_2O_5-SO_3-H_2O$, phase relationships of the system were investigated in this study at 100°C. and 145°C. The ternary system $CaO-SO_3-H_2O$ was investigated at 100°C. and 145°C., and the ternary system $CaO-P_2O_5-H_2O$ system at 145°C.

## Laboratory Work

### Apparatus and method

The solubility relationships were determined in a constant temperature bath in which oil was used to maintain the temperature of 100°C. and a noncombustible heat transfer medium, Arochor 1248 was used for 145°C. The temperature could be controlled with a precision of $\pm$ 0.2°C. for 100°C. and $\pm$ 0.4°C. for 145°C.

The mixtures were continuously rotated at 30 rpm in the constant

temperature bath for seven days. After one week, the mixtures were allowed to settle at the equilibrium temperature for 24 hours.

Liquid samples were taken from the clear solutions. A preheated pipette at 105°C. was used for sampling from the pressure Pyrex bottles. The internal cup sampling shown in Figure 1 and 2 for the pressure bomb was dipped into the solution for sampling and withdrawn immediately thereby separating the liquid sample for analysis later. Solid phase sampling was accomplished by filtering through a preheated sintered glass filter under suction for the 100°C. samples and by filtering through a pressure bomb under suction for the 145°C. samples. The apparatus is shown in Figure 3. All solid samples were washed with anhydrous acetone eight times.

Starting material

The tri-calcium phosphate, di-calcium phosphate and mono-calcium phosphate having formulas corresponding to $Ca_3(PO_4)_2$, $CaHPO_4$ and $Ca(H_2PO_4)_2$ respectively were obtained from the J. T. Baker Chemical Company. Analytical reagent grade phosphoric acid and sulfuric acid were purchased from General Chemical Division, Allied Chemical and Dye Corporation.

Analyses

In the ternary system $CaO-SO_3-H_2O$ only the percentage of CaO and $SO_3$ in the solution were determined. The results of the ternary system $CaO-SO_3-H_2O$ are shown in Tables 1 and 2. In the ternary system $CaO-P_2O_5-H_2O$, the percentages of CaO and $P_2O_5$ were determined and in the quaternary system CaO, $P_2O_5$ and $SO_3$ were determined. The results

Figure 1. Pressure bomb used for 145°C. solubility determinations

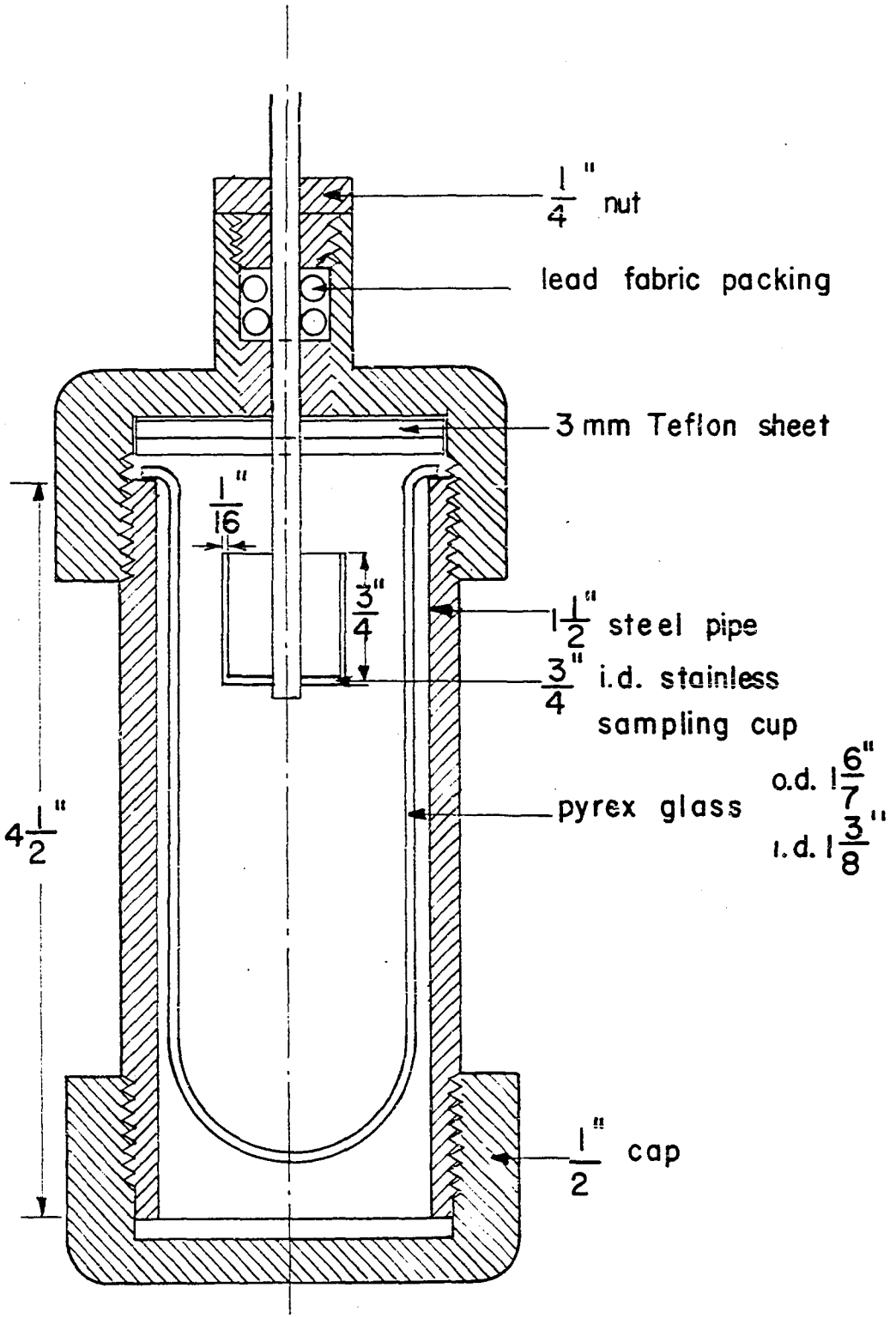

1/4" nut
lead fabric packing
3 mm Teflon sheet
1/16"
3/4"
1 1/2" steel pipe
3/4" i.d. stainless sampling cup
o.d. 1 6/7"
i.d. 1 3/8"
pyrex glass
4 1/2"
1/2" cap

Figure 2. Photograph of pressure bomb use for 145°C. solubility determinations

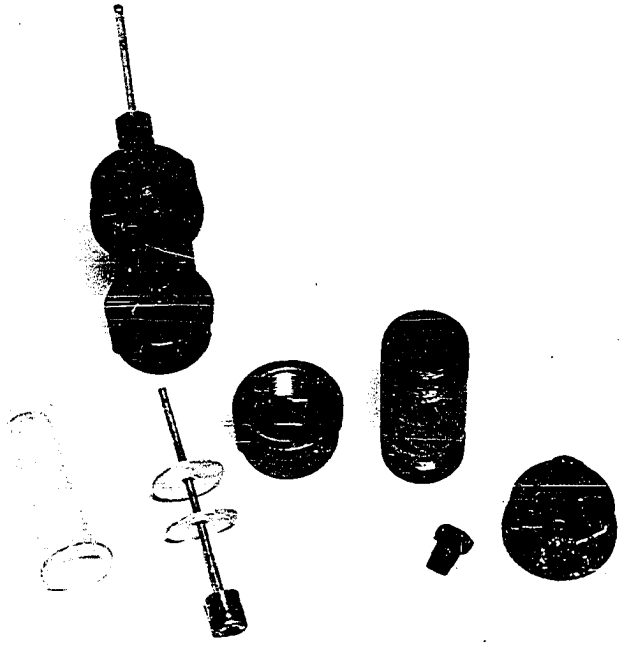


Figure 3. Pressure filtration apparatus

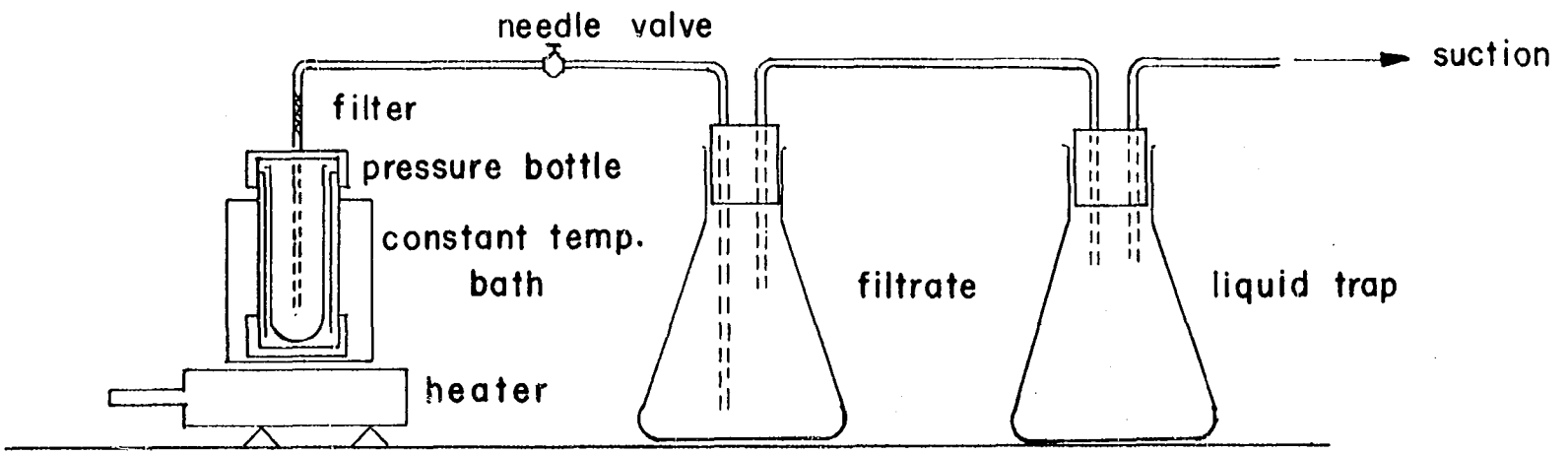

needle valve
suction
filter
pressure bottle
constant temp.
bath
filtrate
liquid trap
heater

Table 1. Equilibrium analyses of the system $CaO-SO_3-H_2O$ at 100°C.

| Sample No. | Material charged[a] $H_2SO_4$ % | Composition of solution in % by weight CaO | $SO_3$ | Value for 100 y[b] | m[b] | Solution saturated with respect to |
|---|---|---|---|---|---|---|
| ES3-1 | 10.2 | 0.256 | 8.81 | 95.5 | 138 | $CaSO_4 \cdot \frac{1}{2}H_2O$ |
| ES3-2 | 14.8 | 0.183 | 11.93 | 98.0 | 98 | $CaSO_4 \cdot \frac{1}{2}H_2O$ |
| ES3-3 | 19.6 | 0.150 | 15.86 | 98.5 | 70 | $CaSO_4 \cdot \frac{1}{2}H_2O$ |
| ES3-4 | 44.8 | 0.090 | 38.21 | 99.5 | 21 | $CaSO_4 \cdot \frac{1}{2}H_2O$, $CaSO_4$ |
| ES3-5 | 65.3 | 0.069 | 52.14 | 99.6 | 12 | $CaSO_4 \cdot \frac{1}{2}H_2O$, $CaSO_4$ |
| ES3-6 | 87.3 | 0.041 | 70.38 | 99.8 | 5.3 | $CaSO_4$ |
| ES3-7 | 94.7 | 0.030 | 76.27 | 99.9 | 4.2 | $CaSO_4$ |

[a] All mixtures were made using 50 c.c. of $H_2SO_4$ of the indicated strength and 5 grams of $CaSO_4$

[b] y and m are moles of $H_6$ and water defined on page 38

of the ternary system $CaO-P_2O_5-H_2O$ and the quaternary system $CaO-P_2O_5-SO_3-H_2O$ are shown in Tables 3, 4 and 5 respectively.

Phosphorus pentoxide was determined by the colorimetric procedure of Bridger, Boylan and Markey (8) after making the solution according to the offical method of the Association of Official Agricultural Chemists (1). Calcium oxide was determined by precipitation as oxalate and by titration of the oxalic acid. Sulfur trioxide was determined

Table 2. Equilibrium analyses of the system $CaO-SO_3-H_2O$ at 145°C.

| Sample No. | Material charged[a] $H_2SO_4$ % | Composition of solution in % by weight CaO | $SO_3$ | Value for 100 y | m | Solution saturated with respect to |
|---|---|---|---|---|---|---|
| ES4-1 | 10.6 | 0.242 | 8.94 | 96.0 | 135 | $CaSO_4 \cdot \frac{1}{2}H_2O$, $CaSO_4$ |
| ES4-2 | 17.4 | 0.209 | 14.07 | 96.1 | 81 | $CaSO_4 \cdot \frac{1}{2}H_2O$, $CaSO_4$ |
| ES4-5 | 45.8 | 0.123 | 37.84 | 99.5 | 21 | $CaSO_4$ |
| ES4-6 | 64.3 | 0.105 | 51.43 | 99.7 | 14 | $CaSO_4$ |
| ES4-7 | 86.2 | 0.090 | 69.55 | 99.7 | 5.8 | $CaSO_4$ |
| ES4-8 | 94.8 | 0.085 | 76.43 | 99.8 | 4.1 | $CaSO_4$ |

[a]All mixtures were made using 50 c.c. of $H_2SO_4$ of the indicated strength and 5 grams of $CaSO_4$

gravimetrically by precipitation as $BaSO_4$. Nitrogen was determined by the ferrous sulfate zinc-soda method (1). All analyses were made in duplicate and with checks using chemical pure reagents.

To determine the nature of the solid phase the rest analysis method (40) was used with the addition of the calcium nitrate as a telltale substance. By this method both the solution and the solid phase can be analyzed. The quantity of adhering liquid in the solid phase was calculated by using a calcium nitrate balance. The solid phases in the quaternary system were determined by X ray diffraction.

Table 3. Equilibrium analyses of the system $CaO-P_2O_5-H_2O$ at 145°C.

| Sample No. | Material charged[a] | | Composition of solution in % by weight | | Value for | | Solution saturated with respect to |
|---|---|---|---|---|---|---|---|
| | $H_3PO_4$ % | $Ca(H_2PO_4)_2 \cdot H_2O$ gm. | CaO | $P_2O_5$ | 100 y | m | |
| EL8-2 | 1.20 | 4.83 | 0.094 | 2.9 | 97.1 | 257 | $CaHPO_4$ |
| EL8-18 | 4.30 | 11.92 | 0.98 | 10.1 | 91.8 | 70 | $CaHPO_4$ |
| EL8-1 | 4.68 | 12.80 | 1.80 | 11.1 | 86.3 | 63 | $CaHPO_4$ |
| EL8-19 | 5.25 | 19.86 | 1.81 | 14.0 | 95.8 | 47 | $CaHPO_4$ |
| EL8-4 | 6.34 | 22.64 | 2.04 | 16.9 | 89.8 | 38 | $CaHPO_4$ |
| EL8-21 | 12.80 | 23.06 | 2.25 | 20.0 | 95.2 | 33 | $CaHPO_4$ |
| EL8-22 | 17.6 | 26.48 | 3.31 | 24.9 | 95.5 | 23 | $CaHPO_4$ |
| EL8-3 | 19.4 | 26.37 | 2.85 | 26.7 | 90.9 | 21 | $CaHPO_4$ |
| EL8-23 | 21.8 | 26.42 | 3.30 | 28.8 | 94.2 | 19 | $CaHPO_4$ |
| EL8-24 | 22.6 | 26.44 | 3.60 | 29.9 | 95.9 | 8.8 | $CaHPO_4$ |
| EL8-16 | 22.7 | 26.48 | 3.74 | 29.9 | 89.4 | 17 | $CaHPO_4$ |

[a] All mixtures were made using 50 c.c. of $H_3PO_4$ of the indicated strength and the indicated weight of $Ca(H_2PO_4)_2 \cdot H_2O$

Table 3. (Continued)

| Sample No. | Material charged[a] $H_3PO_4$ % | Material charged[a] $Ca(H_2PO_4)_2 \cdot H_2O$ gm. | Composition of solution in % by weight CaO | Composition of solution in % by weight $P_2O_5$ | Value for 100 y | Value for m | Solution saturated with respect to |
|---|---|---|---|---|---|---|---|
| EL8-25 | 26.3 | 26.45 | 3.84 | 33.3 | 96.1 | 15 | $CaHPO_4$ |
| EL8-17 | 28.8 | 26.39 | 4.39 | 35.8 | 89.6 | 13 | $CaHPO_4$ |
| EL8-26 | 28.7 | 26.58 | 4.37 | 35.8 | 95.9 | 12 | $CaHPO_4$ |
| EL8-7 | 29.2 | 26.64 | 4.56 | 37.4 | 89.7 | 12 | $CaHPO_4$ |
| EL8-8 | 35.4 | 26.65 | 4.84 | 37.1 | 89.0 | 12 | $CaHPO_4$ |
| EL8-31 | 37.1 | 30.81 | 5.04 | 39.0 | 89.1 | 13 | $CaHPO_4$ |
| EL8-12 | 40.3 | 25.12 | 5.27 | 44.0 | 89.9 | 9 | $CaHPO_4$, $Ca(H_2PO_4)_2$ |
| EL8-11 | 40.3 | 25.43 | 5.30 | 44.1 | 89.9 | 9 | $CaHPO_4$, $Ca(H_2PO_4)_2$ |
| EL8-14 | 43.9 | 25.36 | 5.58 | 45.7 | 89.3 | 8.4 | $CaHPO_4$, $Ca(H_2PO_4)_2$ |
| EL8-27 | 47.4 | 25.35 | 4.37 | 51.6 | 72.2 | 6.7 | $Ca(H_2PO_4)_2$ |
| EL8-29 | 62.5 | 16.34 | 3.21 | 57.1 | 98.1 | 5.5 | $Ca(H_2PO_4)_2$ |
| EL8-30 | 75.6 | 14.21 | 1.81 | 63.1 | 97.5 | 4.4 | $Ca(H_2PO_4)_2$ |
| EL8-32 | 85.0 | 14.36 | 1.35 | 66.6 | 98.3 | 3.8 | $Ca(H_2PO_4)_2$ |

Table 4. Equilibrium analyses of the system $CaO-P_2O_5-SO_3-H_2O$ at 100°C.

| Sample No. | Material charged[a] Solution $H_3PO_4$ % | Solution $H_2SO_4$ % | Solid | Composition of solution in % by weight CaO | $P_2O_5$ | $SO_3$ | Values for 100x | 100y | |
|---|---|---|---|---|---|---|---|---|---|
| ESL6-3 | - | 2.2 | D.[b] | 0.095 | 0.09 | 0.125 | 54.6 | 54.6 | 5 |
| ESL6-2 | - | 2.0 | T. | 0.100 | 0.12 | 0.08 | 72.7 | 45.4 | 5 |
| ESL6-1 | - | 1.8 | T. | 0.113 | 0.16 | 0.11 | 61.2 | 56.2 | 3 |
| ESL6-22 | 34.5 | 3.7 | M. | 0.35 | 4.60 | 0.19 | 97.5 | 93.5 | |
| ESL6-4 | 2.0 | 4.2 | D. | 0.908 | 6.56 | 0.210 | 98.2 | 88.7 | |
| ESL6-13 | 4.2 | 3.7 | D. | 2.04 | 7.6 | 0.04 | 99.8 | 79.3 | |
| ESL6-12 | 5.0 | 3.7 | D. | 0.76 | 8.29 | 0.202 | 99.5 | 98.0 | |
| ESL6-8 | 4.8 | 3.7 | D. | 0.75 | 8.10 | 0.201 | 99.0 | 95.0 | |
| ESL6-5 | 4.1 | 3.7 | D. | 1.22 | 10.36 | 0.206 | 98.8 | 90.4 | |
| ESL6-7 | 6.0 | 3.7 | D. | 1.52 | 12.83 | 0.274 | 98.5 | 87.9 | |
| ESL6-14 | 6.3 | 3.7 | M. | 1.82 | 14.60 | 0.20 | 98.5 | 80.2 | |
| ESL6-19 | 20.8 | 3.7 | M. | 2.62 | 17.80 | 0.15 | 99.5 | 93.7 | |
| ESL6-23 | 2.7 | 3.7 | M. | 3.20 | 21.20 | 0.15 | 99.7 | 87.3 | |
| ESL6-9 | 8.6 | 3.7 | D. | 4.01 | 27.80 | 0.10 | 99.3 | 57.5 | |
| ESL6-24 | 15.3 | 3.7 | D. | 5.13 | 29.80 | 0.09 | 100 | 86.0 | |
| ESL6-16 | 8.2 | 3.7 | M. | 5.88 | 30.80 | 0.09 | 98.5 | 66.0 | |

[a]All mixtures were made using 50 c.c. of solution of indicated composit

[b]D. = $CaHPO_4$, M. = $Ca(H_2PO_4)_2$, M.M. = $Ca(H_2PO_4)_2 \cdot H_2O$, T = $Ca_3(PO_4)_2$, C.

$_2O_5$-$SO_3$-$H_2O$ at 100°C.

| of by $SO_3$ | Values for 100x | 100y | m | Molar ratio $\frac{H}{PO_4}$ | $\frac{CaO}{P_2O_5}$ | Solution saturated with respect to |
|---|---|---|---|---|---|---|
| 0.125 | 54.6 | 54.6 | 5020 | 3.00 | 2.50 | D. C.H. C.D.[b] |
| 0.08 | 72.7 | 45.4 | 5020 | 1.89 | 2.23 | D. C.H. |
| 0.11 | 61.2 | 56.2 | 3450 | 2.76 | 2.14 | D. C.H. C.D. |
| 0.19 | 97.5 | 93.5 | 171 | 2.87 | 0.21 | D. C.H. |
| 0.210 | 98.2 | 88.7 | 120 | 2.71 | 0.34 | D. C.H. |
| 0.04 | 99.8 | 79.3 | 86.3 | 2.38 | 0.63 | D. C.H. |
| 0.202 | 99.5 | 98.0 | 25.5 | 2.96 | 0.06 | D. C.H. |
| 0.201 | 99.0 | 95.0 | 55.5 | 2.88 | 0.15 | D. C.H. |
| 0.206 | 98.8 | 90.4 | 67.2 | 2.74 | 0.30 | D. C.H. |
| 0.274 | 98.5 | 87.9 | 64.2 | 2.68 | 0.36 | D. C.H. |
| 0.20 | 98.5 | 80.2 | 85.7 | 2.44 | 0.60 | D. C.H. C.A. |
| 0.15 | 99.5 | 93.7 | 17.3 | 2.82 | 0.23 | D. C.A. C.H. |
| 0.15 | 99.7 | 87.3 | 27.9 | 2.62 | 0.39 | C. C.A. C.H. |
| 0.10 | 99.3 | 57.5 | 65.8 | 1.74 | 1.28 | D. C.A. C.H. |
| 0.09 | 100 | 86.0 | 17.1 | 2.58 | 0.42 | D. C.A. C.H. |
| 0.09 | 98.5 | 66.0 | 34.1 | 2.02 | 1.03 | D. C.A. C.H. |

ıtion of indicated composition and 10 grams of indicated material

$)_4)_2 \cdot H_2O$, T = $Ca_3(PO_4)_2$, C.A. = $CaSO_4$, C.H. = $CaSO_4 \cdot \frac{1}{2}H_2O$, C.D. = $CaSO_4 \cdot 2H_2O$

Table 4. (Continued)

| Sample No. | Material charged[a] Solution $H_3PO_4$ % | Solution $H_2SO_4$ % | Solid | Composition of solution in % by weight CaO | $P_2O_5$ | $SO_3$ | Values for 100x | 100y | m |
|---|---|---|---|---|---|---|---|---|---|
| ESL6-25 | 24.1 | 3.7 | D.[b] | 6.20 | 32.50 | 0.08 | 100 | 84.0 | 14.8 |
| ESL6-17 | 16.8 | 3.7 | M. | 6.60 | 36.00 | 0.12 | 99.8 | 82.1 | 14.6 |
| ESL6-26 | 30.8 | 3.7 | M. | 7.10 | 37.5 | 0.07 | 100 | 84.0 | 11.7 |
| ESL6-28 | 36.2 | 3.7 | M. | 6.50 | 40.1 | 0.06 | 100 | 80.6 | 10.5 |
| ESL6-29 | 37.4 | 3.7 | M. | 5.50 | 42.9 | 0.06 | 100 | 89.0 | 9.3 |
| ESL6-30 | 38.6 | 3.7 | M. | 5.00 | 45.1 | 0.04 | 100 | 90.4 | 8.1 |
| ESL6-31 | 38.8 | 3.7 | M. | 4.20 | 47.2 | 0.04 | 100 | 92.4 | 8.3 |
| ESL6-20 | 14.2 | 3.7 | D. | 3.08 | 51.3 | 0.04 | 100 | 92.8 | 6.3 |
| ESL6-21 | 30.4 | 3.7 | D. | 2.74 | 55.2 | - | 100 | 95.4 | 6.3 |
| ESL6-32 | 40.9 | 3.7 | M. | 1.90 | 56.5 | - | 100 | 97.3 | 5.3 |
| ESL6-33 | 50.6 | 3.7 | M. | 1.70 | 58.4 | - | 100 | 98.0 | 5.3 |
| ESL6-34 | 53.8 | 3.7 | M. | 0.91 | 62.6 | - | 100 | 98.7 | 4.3 |
| ESL6-35 | 55.1 | 3.7 | M. | 0.52 | 65.2 | - | 100 | 97.2 | 4.3 |
| ESL6-36 | 56.8 | 3.7 | M. | 0.30 | 67.6 | - | 100 | 99.6 | 3.3 |

| ;ion of in % by ght | | Values for | | | Molar ratio | | Solution saturated with respect to | |
|---|---|---|---|---|---|---|---|---|
| $^{2}O_5$ | $SO_3$ | 100x | 100y | m | $\frac{H}{PO_4}$ | $\frac{CaO}{P_2O_5}$ | | |
| 2.50 | 0.08 | 100 | 84.0 | 14.8 | 2.52 | 0.48 | D. C.A. | C.H.[b] |
| 6.00 | 0.12 | 99.8 | 82.1 | 14.6 | 2.47 | 0.54 | D. C.A. | C.H. |
| 7.5 | 0.07 | 100 | 84.0 | 11.7 | 2.52 | 0.48 | D. C.A. | |
| 0.1 | 0.06 | 100 | 80.6 | 10.5 | 2.42 | 0.58 | D. M.M. | C.A. |
| 2.9 | 0.06 | 100 | 89.0 | 9.5 | 2.66 | 0.34 | D. M.M. | C.A. |
| 5.1 | 0.04 | 100 | 90.4 | 8.7 | 2.71 | 0.29 | M.M. | C.A. |
| 7.2 | 0.04 | 100 | 92.4 | 8.1 | 2.77 | 0.23 | M.M. | C.A. |
| 1.3 | 0.04 | 100 | 92.8 | 6.5 | 2.78 | 0.22 | M.M. | C.A. |
| 5.2 | - | 100 | 95.4 | 6.0 | 2.86 | 0.14 | M.M. | C.A. |
| 6.5 | - | 100 | 97.3 | 5.8 | 2.92 | 0.08 | M. | C.A. |
| 8.4 | - | 100 | 98.0 | 5.4 | 2.94 | 0.06 | M. | C.A. |
| 2.6 | - | 100 | 98.7 | 4.6 | 2.96 | 0.04 | M. | C.A. |
| 5.2 | - | 100 | 97.2 | 4.1 | 2.91 | 0.09 | M. | C.A. |
| 7.6 | - | 100 | 99.6 | 3.7 | 2.99 | 0.01 | M. | C.A. |

Table 5. Equilibrium analyses of the system $CaO-P_2O_5-SO_3-H_2O$ at 145°C.

| Sample No. | Material charged[a] Solution $H_3PO_4$ % | Solution $H_2SO_4$ % | Solid | Composition of solution in % by weight CaO | $P_2O_5$ | $SO_3$ | Values for 100x | 100y | |
|---|---|---|---|---|---|---|---|---|---|
| ESL10-1 | - | 2.4 | T.[b] | 0.14 | 0.44 | 0.16 | 81.0 | 79.2 | 144 |
| ESL10-13 | - | 4.4 | T. | 0.24 | 1.73 | 0.43 | 87.2 | 89.8 | 37 |
| ESL10-14 | - | 6.7 | T. | 0.26 | 2.14 | 0.52 | 91.5 | 91.3 | 30 |
| ESL10-2 | - | 8.9 | T. | 0.48 | 3.88 | 0.57 | 90.7 | 90.5 | 17 |
| ESL10-15 | - | 11.1 | T. | 0.51 | 4.02 | 0.61 | 92.0 | 90.2 | 17 |
| ESL10-16 | 4.6 | 3.75 | D. | 1.01 | 6.15 | 0.83 | 89.0 | 83.7 | 10 |
| ESL10-3 | 10.0 | 3.75 | D. | 1.53 | 12.70 | 1.02 | 95.5 | 90.5 | 5 |
| ESL10-17 | 13.7 | 3.75 | D. | 1.67 | 13.50 | 1.04 | 99.5 | 90.2 | 4 |
| ESL10-18 | 21.2 | 3.75 | D. | 1.82 | 14.90 | 1.07 | 96.0 | 90.0 | 4 |
| ESL10-4 | 28.4 | 3.75 | D. | 1.90 | 15.30 | 1.21 | 95.5 | 90.5 | 4 |
| ESL10-19 | 30.0 | 3.75 | D. | 2.01 | 16.40 | 1.24 | 95.7 | 90.2 | 3 |
| ESL10-5 | 40.0 | 3.75 | D. | 2.27 | 18.40 | 1.25 | 96.0 | 90.0 | 3 |
| ESL10-6 | 41.5 | 3.75 | D. | 2.28 | 18.65 | 1.25 | 96.4 | 90.2 | 3 |
| ESL10-20 | 41.5 | 3.75 | D. | 2.28 | 18.70 | 1.25 | 96.3 | 90.2 | 3 |
| ESL10-7 | 45.0 | 3.75 | D. | 3.25 | 28.30 | 1.27 | 97.8 | 91.2 | 1 |
| ESL10-8 | 46.0 | 3.75 | M. | 3.27 | 28.76 | 1.27 | 96.6 | 90.7 | 1 |

[a]All mixtures were made using 50 c.c. of solution of indicated composition

[b]D. = $CaHPO_4$, M. = $Ca(H_2PO_4)_2$, M.M. = $Ca(H_2PO_4)_2 \cdot H_2O$, T = $Ca_3(PO_4)_2$, C.A. =

CaO-$P_2O_5$-$SO_3$-$H_2O$ at 145°C.

| sition of on in % by eight | | Values for | | | Molar ratio | | Solution saturated with respect to |
|---|---|---|---|---|---|---|---|
| $P_2O_5$ | $SO_3$ | 100x | 100y | m | $\frac{H}{PO_4}$ | $\frac{CaO}{P_2O_5}$ | |
| 0.44 | 0.16 | 81.0 | 79.2 | 1440 | 2.93 | 0.77 | D. C.H.[b] |
| 1.73 | 0.43 | 87.2 | 89.8 | 379 | 3.08 | 0.37 | D. C.H. |
| 2.14 | 0.52 | 91.5 | 91.3 | 300 | 2.99 | 0.29 | D. C.H. |
| 3.88 | 0.57 | 90.7 | 90.5 | 177 | 2.99 | 0.32 | D. C.H. |
| 4.02 | 0.61 | 92.0 | 90.2 | 170 | 2.94 | 0.332 | D. C.H. |
| 6.15 | 0.83 | 89.0 | 83.7 | 105 | 2.82 | 0.396 | D. C.H. |
| 12.70 | 1.02 | 95.5 | 90.5 | 50 | 2.84 | 0.30 | D. C.H. C.A. |
| 13.50 | 1.04 | 99.5 | 90.2 | 47 | 2.72 | 0.29 | D. C.H. C.A. |
| 14.90 | 1.07 | 96.0 | 90.0 | 42 | 2.81 | 0.31 | D. C.H. |
| 15.30 | 1.21 | 95.5 | 90.5 | 40 | 2.84 | 0.30 | D. C.H. C.A. |
| 16.40 | 1.24 | 95.7 | 90.2 | 37 | 2.82 | 0.31 | D. C.H. C.A. |
| 18.40 | 1.25 | 96.0 | 90.0 | 32 | 2.81 | 0.31 | D. C.H. C.A. |
| 18.65 | 1.25 | 96.4 | 90.2 | 32 | 2.80 | 0.31 | D. C.H. C.A. |
| 18.70 | 1.25 | 96.3 | 90.2 | 32 | 2.80 | 0.32 | D. C.H. C.A.M. |
| 28.30 | 1.27 | 97.8 | 91.2 | 18 | 2.80 | 0.27 | D. C.H. C.A. |
| 28.76 | 1.27 | 96.6 | 90.7 | 17 | 2.82 | 0.28 | D. C.H. C.A.M. |

solution of indicated composition and 10 grams of indicated material

$(H_2PO_4)_2 \cdot H_2O$, T = $Ca_3(PO_4)_2$, C.A. = $CaSO_4$, C.H. = $CaSO_4 \cdot \frac{1}{2}H_2O$, C.D. = $CaSO_4 \cdot 2H_2O$

Table 5. (Continued)

| Sample No. | Material charged[a] Solution $H_3PO_4$ % | Solution $H_2SO_4$ % | Solid | Composition of solution in % by weight CaO | $P_2O_5$ | $SO_3$ | Values for 100x | 100y |
|---|---|---|---|---|---|---|---|---|
| ESL10-21 | 54.0 | 3.75 | M.[b] | 4.19 | 36.70 | 1.10 | 98.2 | 90.5 |
| ESL10-9 | 56.2 | 3.75 | M. | 5.02 | 43.10 | 0.75 | 99.2 | 90.6 |
| ESL10-22 | 61.4 | 3.75 | M. | 5.51 | 47.60 | 0.47 | 99.4 | 90.8 |
| ESL10-10 | 64.3 | 3.75 | M. | 5.50 | 47.10 | 0.51 | 99.4 | 90.2 |
| ESL10-11 | 66.8 | 3.75 | M. | 4.27 | 51.00 | 0.27 | 99.7 | 93.0 |
| ESL10-12 | 70.1 | 3.75 | M. | 3.51 | 53.68 | 0.13 | 99.8 | 94.6 |
| ESL10-23 | 72.4 | 3.75 | M. | 3.21 | 56.04 | 0.05 | 99.8 | 95.2 |
| ESL10-24 | 76.8 | 3.75 | M. | 2.34 | 60.31 | - | 100 | 96.7 |
| ESL10-25 | 80.2 | 3.75 | M. | 1.06 | 64.46 | - | 100 | 98.6 |

| ıtion of ı in % by ght | | Values for | | | Molar ratio | | Solution saturated with respect to |
|---|---|---|---|---|---|---|---|
| $P_2O_5$ | $SO_3$ | 100x | 100y | m | $\frac{H}{PO_4}$ | $\frac{CaO}{P_2O_5}$ | |
| 5.70 | 1.10 | 98.2 | 90.5 | 9.6 | 2.76 | 0.39 | D. C.A.[b] |
| 3.10 | 0.75 | 99.2 | 90.6 | 6.3 | 2.74 | 0.28 | D. C.A. |
| 7.60 | 0.47 | 99.4 | 90.8 | 4.96 | 2.74 | 0.28 | D. M. C.A. |
| 7.10 | 0.51 | 99.4 | 90.2 | 5.11 | 2.72 | 0.30 | D. M. C.A. |
| 1.00 | 0.27 | 99.7 | 93.0 | 4.07 | 2.80 | 0.21 | M. C.H. C.A. |
| 3.68 | 0.13 | 99.8 | 94.6 | 3.42 | 2.84 | 0.16 | M. C.A. |
| 6.04 | 0.05 | 99.8 | 95.2 | 2.87 | 2.86 | 0.14 | M. C.A. |
| 0.31 | - | 100 | 96.7 | 2.01 | 2.90 | 0.099 | M. C.A. |
| 4.46 | - | 100 | 98.6 | 1.52 | 2.95 | 0.044 | M. C.A. |

Graphical representation

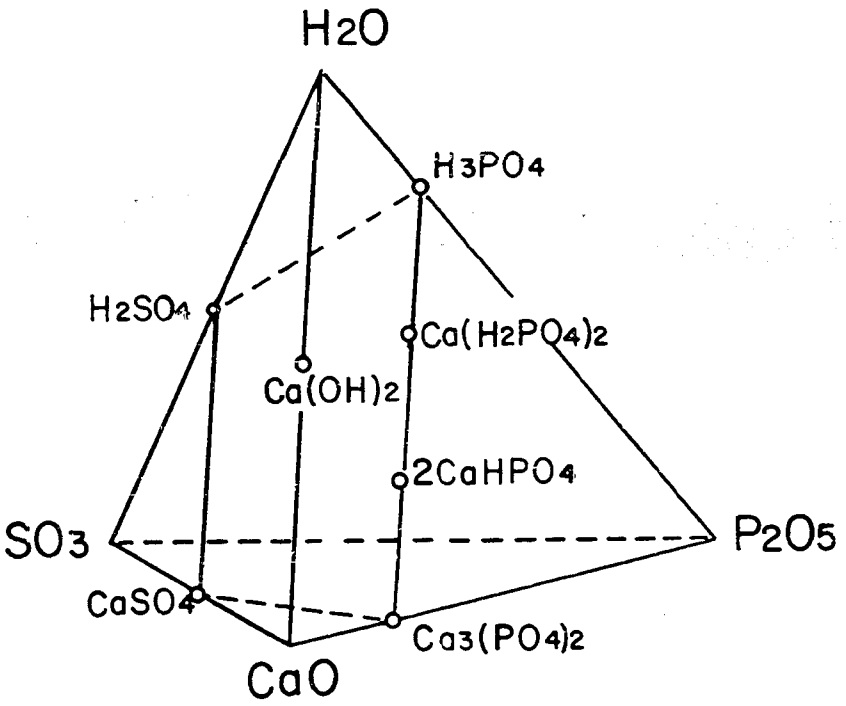
Graphical representation of four components is very difficult. It may be accomplished however, by using an isothermal solid model. The construction of such a model makes use of the geometrical properties of the regular tetrahedron. The four corners in the tetrahedron are used to represent the mole percent of compounds of CaO, $P_2O_5$, $SO_3$ and $H_2O$.

If the four corners of the regular tetrahedron represent directly the mole percent of CaO, $P_2O_5$, $SO_3$ and $H_2O$, $CaSO_4$, $Ca_3(PO_4)_2$, $H_2SO_4$ and $H_3PO_4$ lie in a plane and lines joining them form a trapezoid as shown in Figure 4. If the corners in the regular tetrahedron represent the mole percent of the components $(CaO)_3$, $(SO_3)_3$, $P_2O_5$, $(H_2O)_3$, the plane joining the compounds $Ca_3(SO_4)_3$, $Ca_3(PO_4)_2$, $H_6(SO_4)_3$ and $H_6(PO_4)_2$ forms a square as shown in Figure 5. $H_2O$ is expressed as moles per two moles total of $Ca_3(SO_4)_3$, $H_6(SO_4)_3$, $H_6(PO_4)_2$ and $Ca_3(PO_4)_2$ is plotted vertically above the $Ca_3(SO_4)_3$, $H_6(SO_4)_3$, $H_6(PO_4)_2$ and $Ca_3(PO_4)_2$ base forming an upright prism. Figures 6 and 7 show the resulting model.

In order to indicate a solution in the diagram, the coordinates determining the position on the square base and the height above the base must be determined. The position in the square base represents the mutual relationship between the amounts of $Ca_3(SO_4)_3$, $H_6(SO_4)_3$, $Ca_3(PO_4)_2$ and $H_6(PO_4)_2$. The position above the base represents the water content.

The experimental data give the composition of the solution as weight percent of CaO, $P_2O_5$, $SO_3$ and $H_2O$ (by difference). $Ca_3$,

Figure 4. $CaO-P_2O_5-SO_3-H_2O$ system as a regular tetrahedron model showing trapezoidal planer relationship of the major compounds


H2O
H3PO4
H2SO4
Ca(H2PO4)2
Ca(OH)2
2CaHPO4
SO3
P2O5
CaSO4
Ca3(PO4)2
CaO

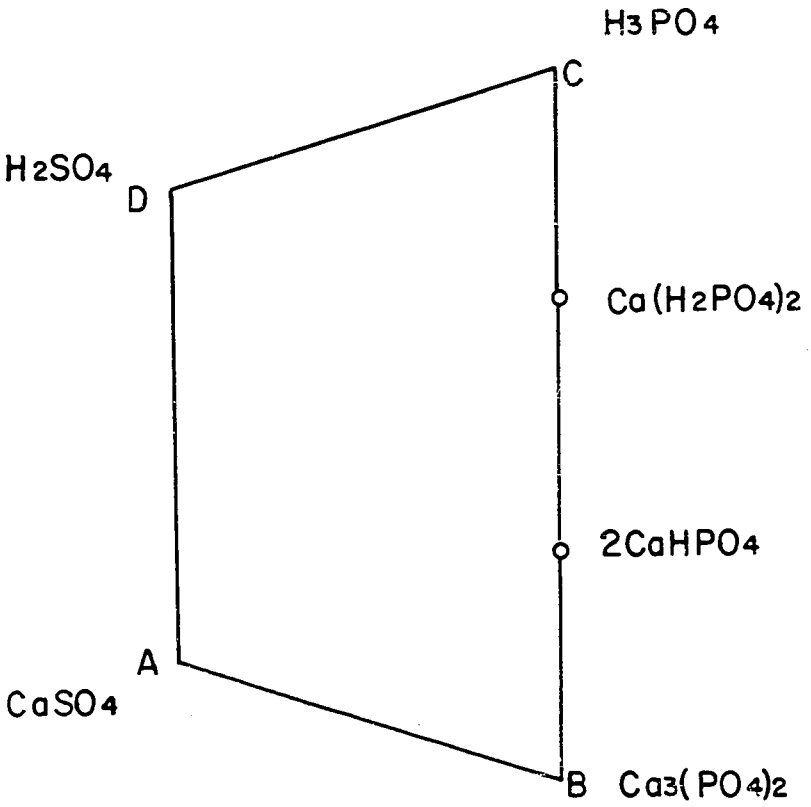
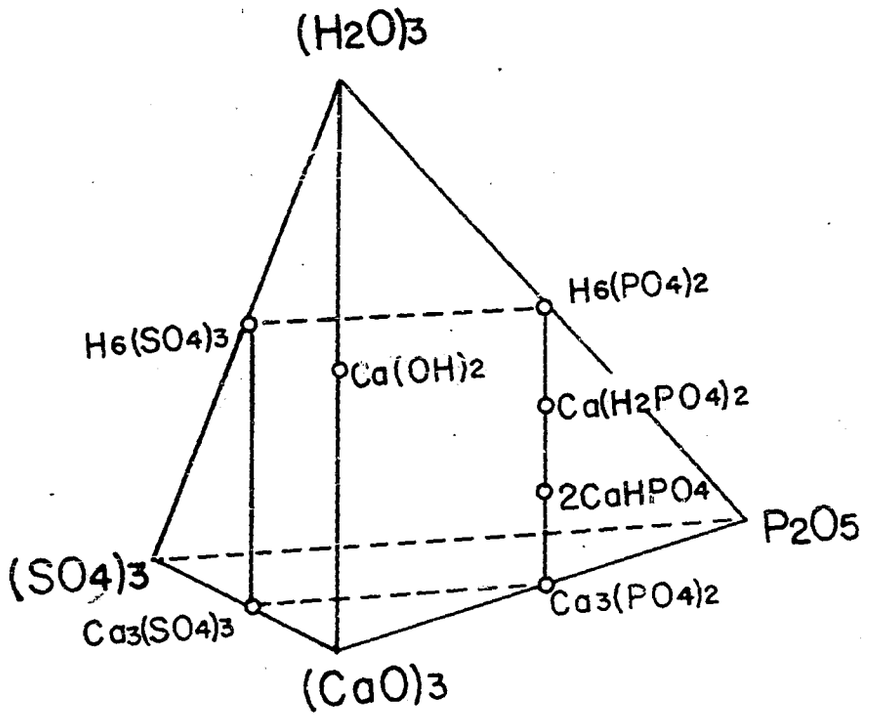

H3PO4
C
H2SO4
D
Ca(H2PO4)2
2CaHPO4
A
CaSO4
B
Ca3(PO4)2

Figure 5. $(CaO)_3$-$(P_2O_5)$-$(SO_3)_3$-$(H_2O)_3$ system as a regular tetrahedron model showing square planer relationship of the major compounds


(H2O)3
H6(PO4)2
H6(SO4)3
Ca(OH)2
Ca(H2PO4)2
2CaHPO4
P2O5
(SO4)3
Ca3(PO4)2
Ca3(SO4)3
(CaO)3

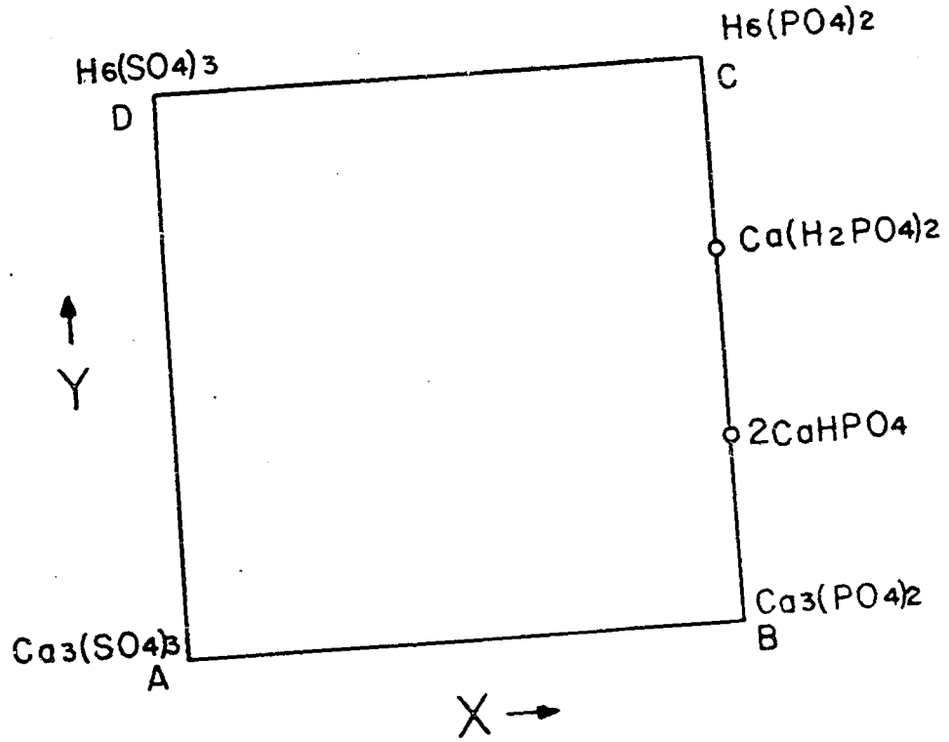
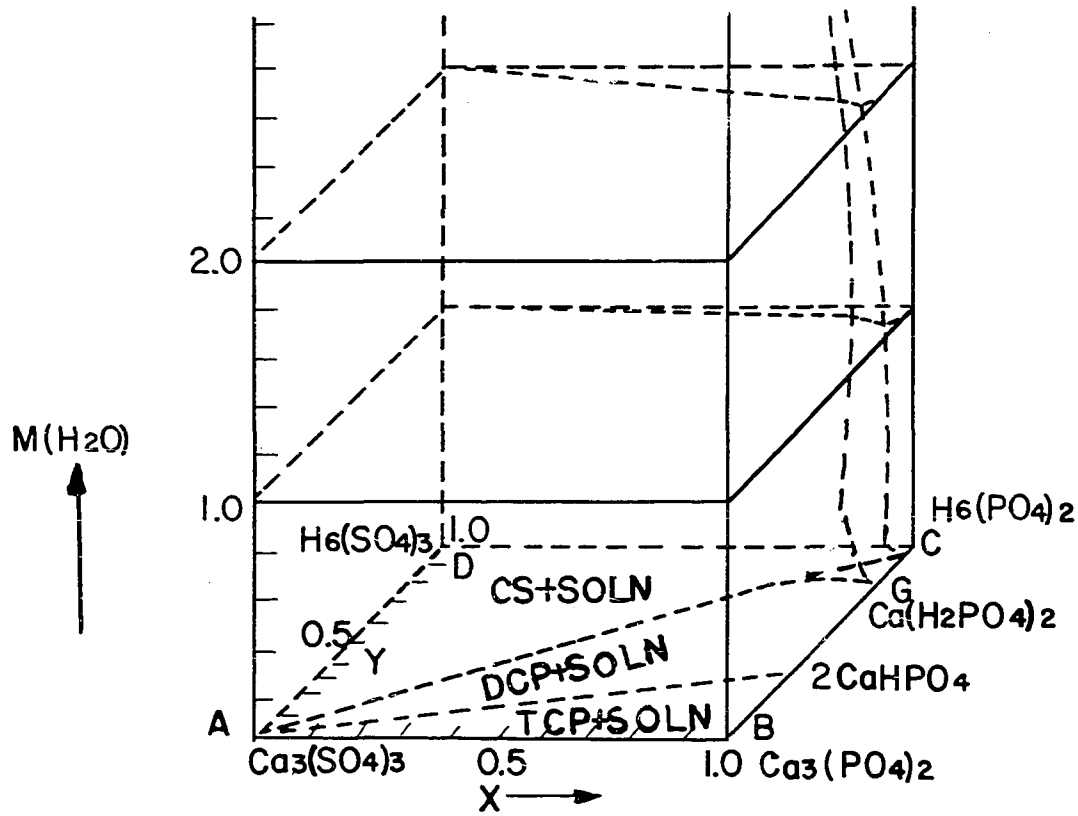

H6(PO4)2
H6(SO4)3
C
D
Ca(H2PO4)2
Y
2CaHPO4
Ca3(PO4)2
B
Ca3(SO4)3
A
X

Figure 6. The modified $CaO-P_2O_5-SO_3-H_2O$ model in space


M(H2O)
2.0
1.0
H6(SO4)3
1.0
D
CS+SOLN
0.5
Y
DCP+SOLN
TCP+SOLN
A
B
C
G
H6(PO4)2
Ca(H2PO4)2
2CaHPO4
Ca3(SO4)3
0.5
1.0 Ca3(PO4)2
X

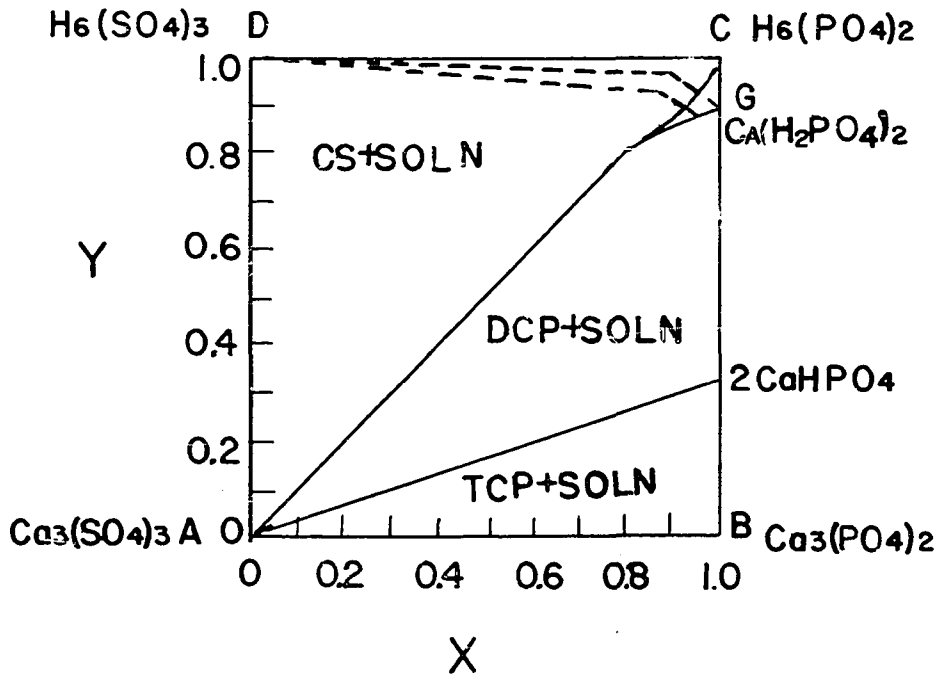
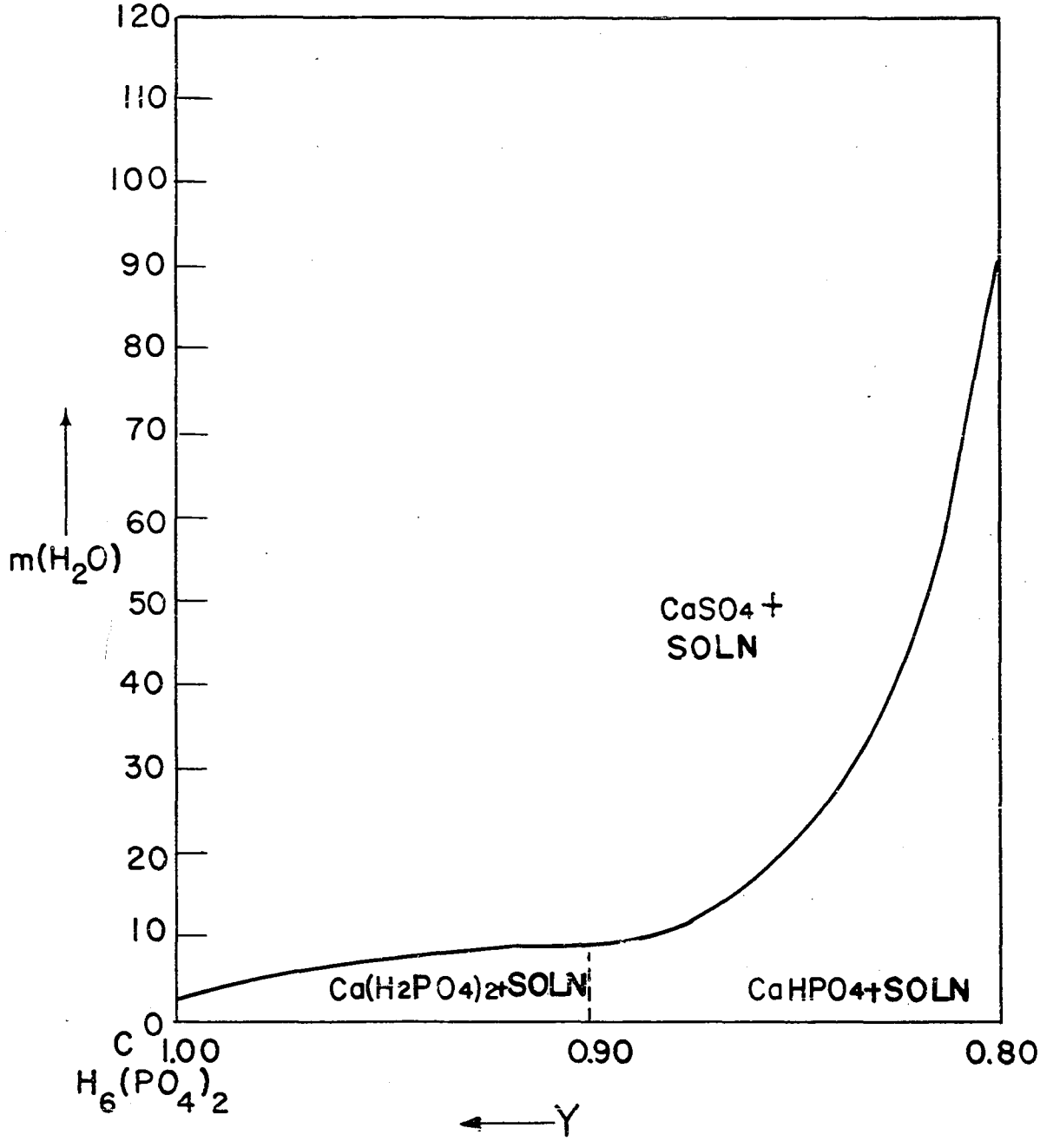

H6(SO4)3 D
C H6(PO4)2
1.0
G
CA(H2PO4)2
0.8
CS+SOLN
Y
0.6
DCP+SOLN
0.4
2CaHPO4
0.2
TCP+SOLN
Ca3(SO4)3 A 0
B Ca3(PO4)2
0 0.2 0.4 0.6 0.8 1.0
X

Figure 7. The modified $CaO-P_2O_5-H_2O$ diagram


120
110
100
90
80
70
60
50
40
30
20
10
0
m(H2O)
CaSO4 + SOLN
Ca(H2P O4)2+SOLN
CaHPO4+SOLN
C 1.00
H6(PO4)2
0.90
0.80
Y

$(SO_3)_3$, $(PO_4)_2$ and $H_6$ are calculated from the percent of CaO, $SO_3$, $P_2O_5$ and $H_2O$. If the amount of $(PO_4)_2$ is specified as x moles, of $(SO_3)_3$ as 1-x moles, of $H_6$ as y moles, and of $Ca_3$ as 1-y moles, the total amount is therefore 2 moles. The amount of water, m, which is not contained in the constituting water of the sulfuric acid and phosphoric acid is then expressed as moles per 2 moles of total $(PO_4)_2$, $(SO_3)_3$, $H_6$ and $Ca_3$.

The composition is then given as: x $(PO_4)_2$, (1-x)$(SO_3)_3$, y$H_6$, (1-y)$Ca_3$, m$H_2O$. An example of the calculation of x, y and m starting from the analysis of a solution weight percent of CaO, $P_2O_5$ and $SO_3$ is given in Appendix.

Since the solubility of $CaSO_4$ in the solution is very small, another method of presenting the data is to omit $SO_3$ and assume that all points represented on the diagram are saturated with or in equilibrium with $SO_3$. Such a diagram can be plotted as a ternary system as shown in Figure 8 for 100°C., and for 145°C. in Figure 9 with and without sulfate.

Figure 8. Field of stability of calcium phosphates with and without sulfate at 100°C.

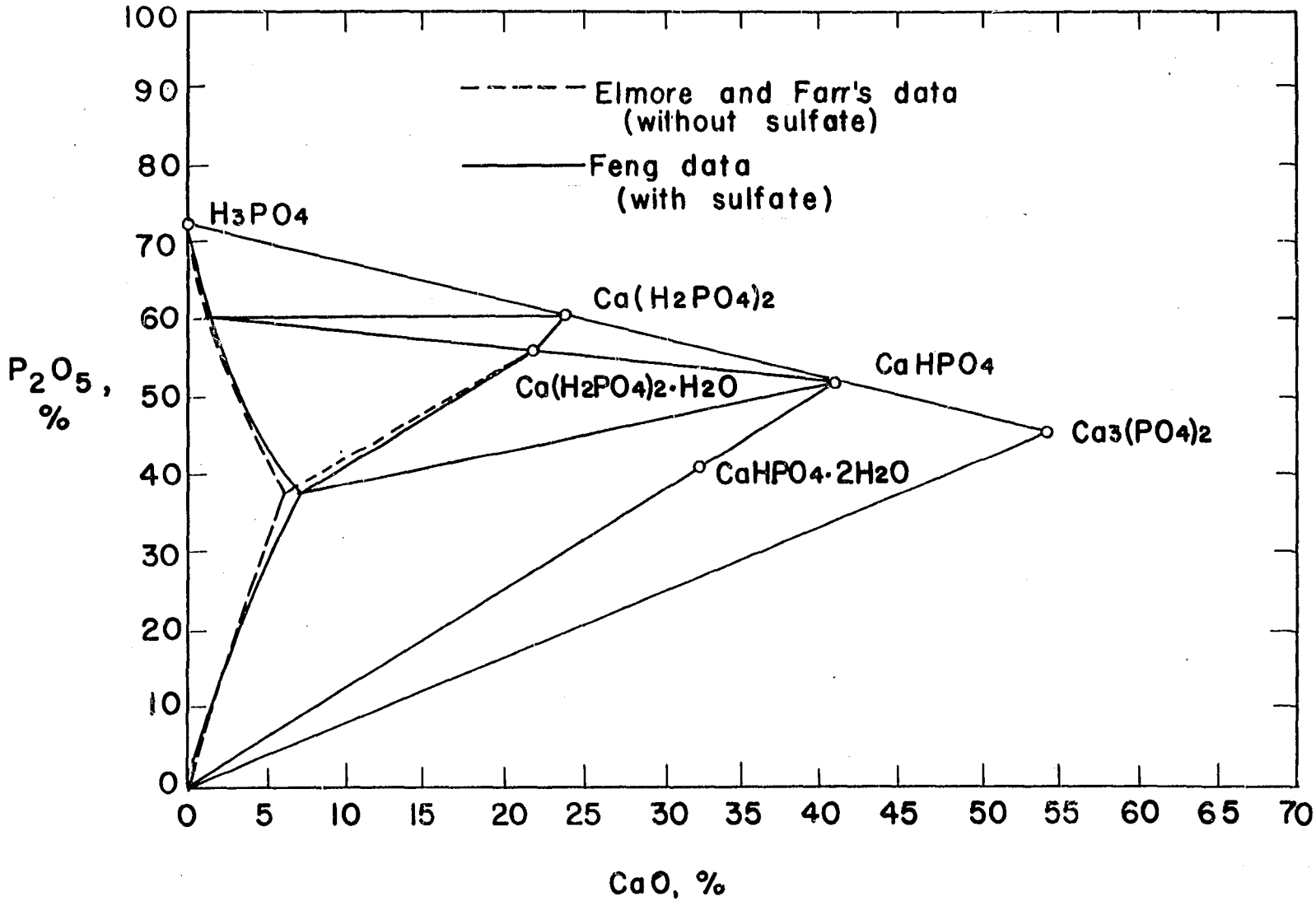
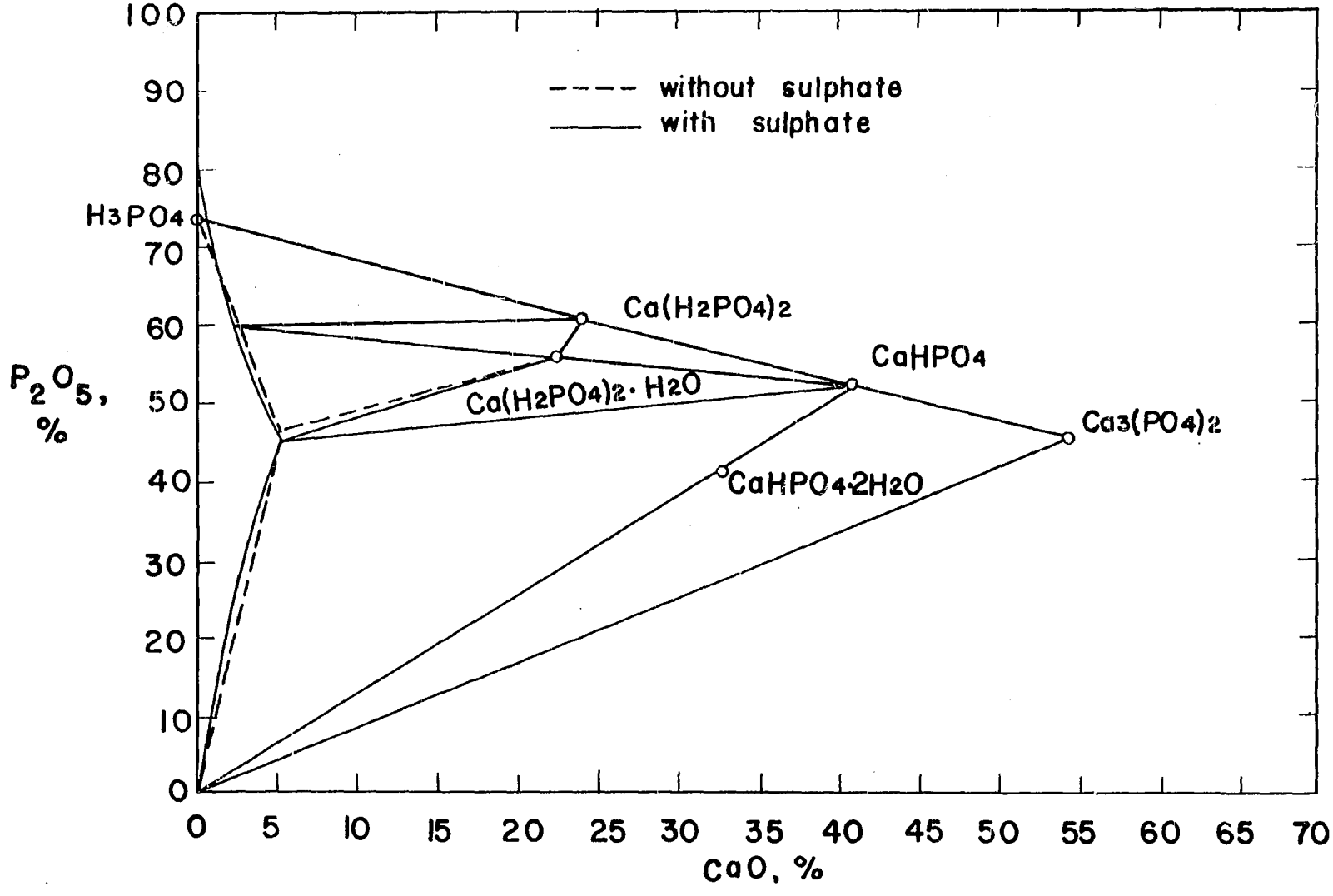

Elmore and Farr's data
(without sulfate)
Feng data
(with sulfate)
H3PO4
Ca(H2PO4)2
Ca(H2PO4)2·H2O
CaHPO4
Ca3(PO4)2
CaHPO4·2H2O
P2O5, %
CaO, %
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70

Figure 9. Field of stability of calcium phosphates with and without sulfate at 145°C.


100
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70
$P_2O_5$, %
CaO, %
---- without sulphate
—— with sulphate
$H_3PO_4$
$Ca(H_2PO_4)_2$
$CaHPO_4$
$Ca(H_2PO_4)_2 \cdot H_2O$
$Ca_3(PO_4)_2$
$CaHPO_4 2H_2O$

## APPLICATION TO DI-CALCIUM PHOSPHATE PROCESS

The square base of the solid model of the phase diagram at 145°C. and 100°C. has been plotted in Figures 11 and 11a respectively. This diagram can be used to propose a process for the preparation of di-calcium phosphate, indicated in Figure 10 by dotted line. In the diagram composition Q represents a saturated solution with respect to di-calcium phosphate at 145°C. Sulfuric acid may be added to this solution until the composition R is reached, the ratio of sulfuric acid to solution Q being QR/DR. Most of calcium sulfate will be immediately precipitated and the composition of the solution becomes S. Phosphate rock can then be added to the solution S until composition T is obtained, where di-calcium phosphate precipitates and the composition of the solution again becomes Q. The amount of sulfuric acid and phosphate rock per cycle converted to di-calcium phosphate and calcium sulfate corresponds to the equation:

$$Ca_{10}F_2(PO_4)_6 + 3H_2SO_4 = 6CaHPO_4 + 3CaSO_4 + CaF \qquad (23)$$

This represents a considerable saving in the consumption of sulfuric acid over that required to produce mono-calcium phosphate in the normal superphosphate processes. Reaction 23 shows a theoretical acid consumption of 1.0 mol $H_2SO_4$ per mol of $P_2O_5$. The normal superphosphate process requires theoretical consumption of 2.0 as shown by the reaction 24.

$$Ca_{10}F_2(PO_4)_6 + 6H_2SO_4 = 3CaH_2(PO_4)_2 + 6CaSO_4 + CaF_2 \qquad (24)$$

Figure 10. Phase equilibria of quaternary system $CaO-P_2O_5-SO_3-H_2O$

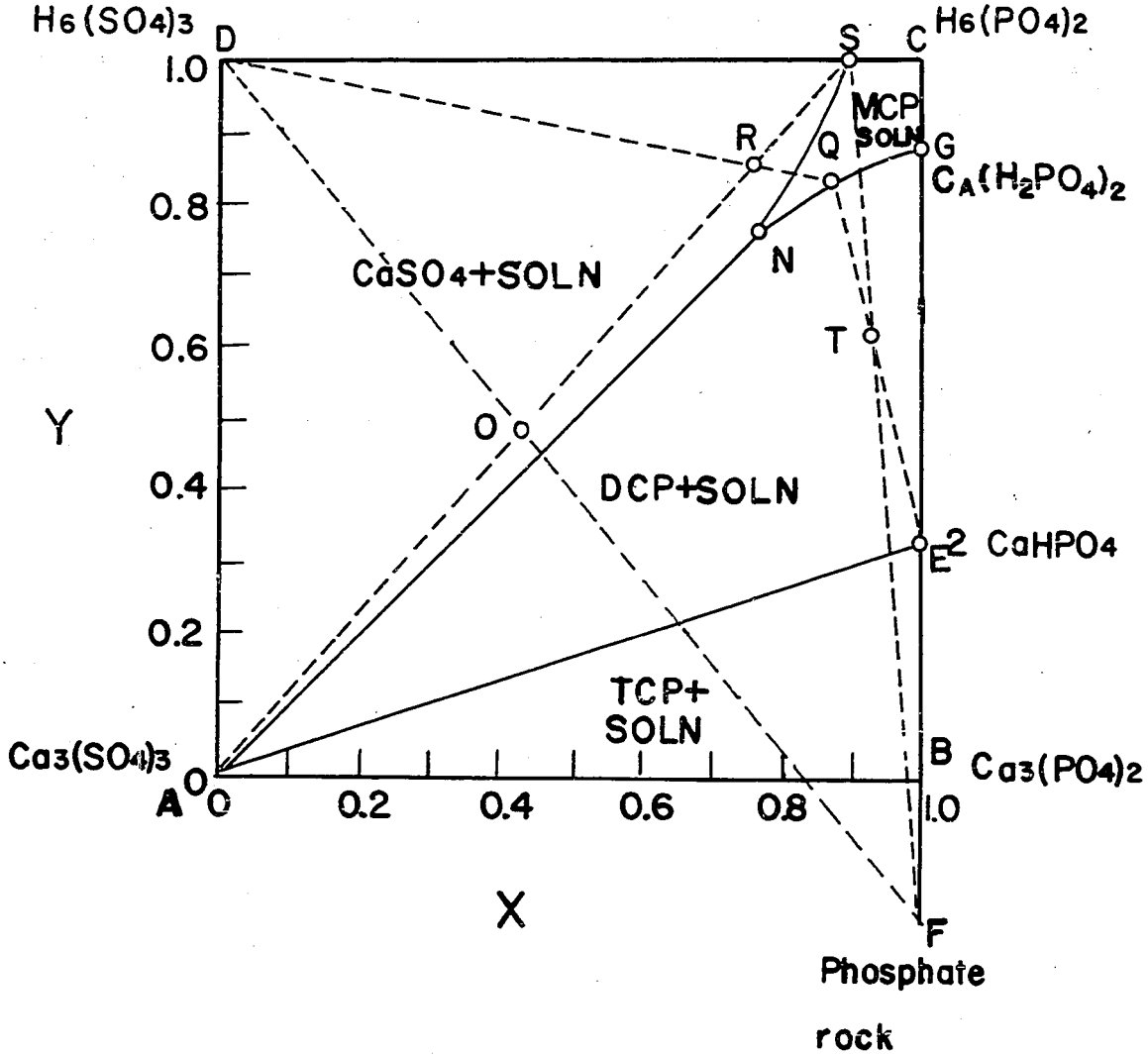

H6(SO4)3
D
S
C
H6(PO4)2
1.0
MCP SOLN
R
Q
G
CA(H2PO4)2
0.8
CaSO4+SOLN
N
T
0.6
Y
O
0.4
DCP+SOLN
E
2 CaHPO4
0.2
TCP+ SOLN
Ca3(SO4)3
O
B
Ca3(PO4)2
A
0
0.2
0.4
0.6
0.8
1.0
X
F
Phosphate rock

Figure 11. Phase equilibria of quaternary system $CaO-P_2O_5-SO_3-H_2O$ at 145°C.

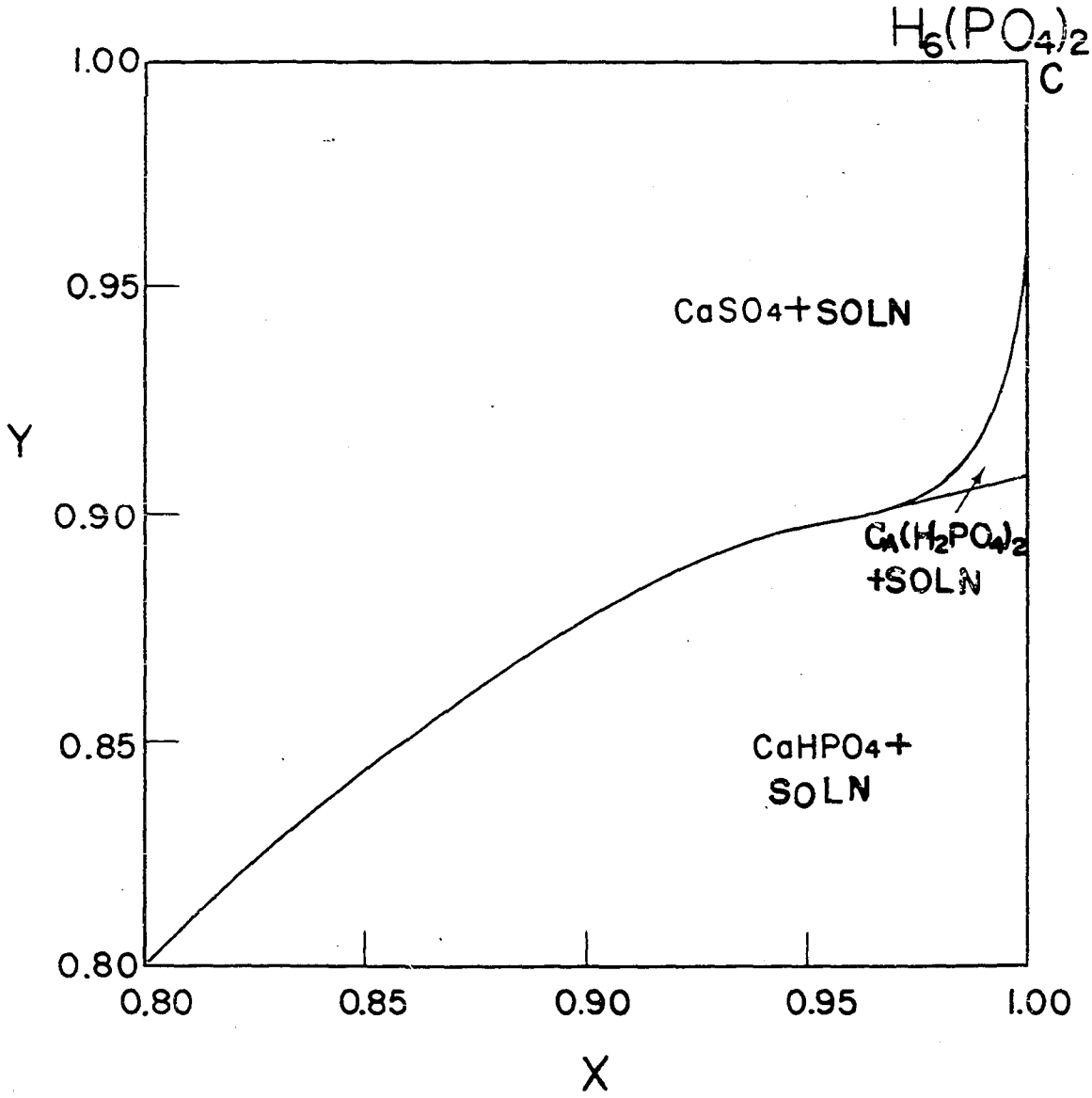
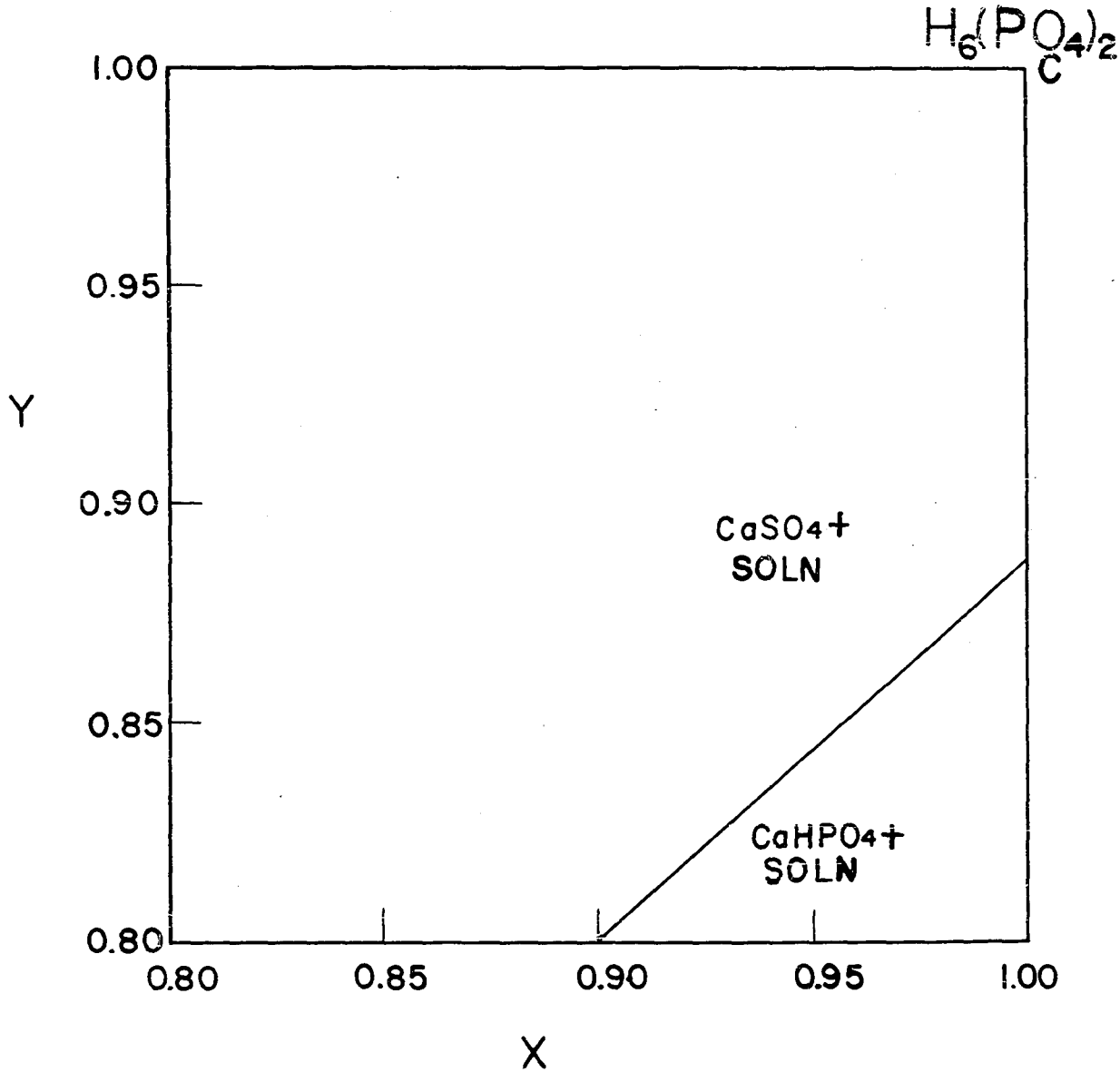

$H_6(PO_4)_2$
C
1.00
0.95
0.90
0.85
0.80
Y
CaSO4+SOLN
$Ca(H_2PO_4)_2$
+SOLN
CaHPO4+
SOLN
0.80
0.85
0.90
0.95
1.00
X

Figure 11a. Phase equilibria of quaternary system $CaO-P_2O_5-SO_3-H_2O$ at 100° C.


$H_6(PO_4)_2$
C
1.00
0.95
0.90
0.85
0.80
Y
CaSO4+
SOLN
CaHPO4+
SOLN
0.80
0.85
0.90
0.95
1.00
X

In addition to the theoretical acid consumption in the reaction 24 some acid is consumed by reaction with the impurities in the phosphate rock. In practice this amounts to about 0.6 mol of acid per mol of $P_2O_5$. In applying the cyclic process, there are theoretically required 1.6 moles of acid per mol of $P_2O_5$. This means that the amount of sulfuric acid required would be 61.5 percent as great as that necessary for normal superphosphate process used.

Since the point Q in Figure 10 is not fixed, it can be set as favorable as possible. The point Q is determined by the amount of the product which is produced per liter of solution per cycle. Actually it will depend on the rate of conversion from phosphate rock to di-calcium phosphate.

## Yield

From Figure 10, the composition R is equal to sulfuric acid and solution Q according to the ratio QR/RD or calcium sulfate and solution S according to the ratio SR/RA.

Therefore the mixture having composition R is equal to

$$\overline{QR} \text{ moles of } H_6(SO_4)_3 + \overline{RD} \text{ moles of solution Q}$$
$$= \overline{SR} \text{ moles of } Ca_3(SO_4)_3 + \overline{RA} \text{ moles of solution S}$$

on the basis of a mixture containing 1.0 mol total having composition R

$$\frac{\overline{QR}}{\overline{QD}} \text{ moles of } H_6(SO_4)_3 + \frac{\overline{RD}}{\overline{QD}} \text{ moles of solution Q}$$
$$= \frac{\overline{SR}}{\overline{SA}} \text{ moles of } Ca_3(SO_4)_3 + \frac{\overline{RA}}{\overline{SA}} \text{ moles of solution S}$$

$$\frac{X_Q - X_R}{X_Q} \text{ moles of } H_6(SO_4)_3 + \frac{X_R}{X_Q} \text{ moles of solution Q} =$$

$$\frac{X_S - X_R}{X_S} \text{ moles of } Ca_3(SO_4)_3 + \frac{X_R}{X_S} \text{ moles of solution S} \qquad (25)$$

For the same reason, a mixture based on one mole of composition T corresponds to

$$\frac{X_T - X_S}{1 - X_S} \text{ moles of rock} + \frac{1 - X_T}{1 - X_S} \text{ moles of solution S} =$$

$$\frac{X_T - X_Q}{1 - X_Q} \text{ moles of } CaHPO_4 + \frac{1 - X_T}{1 - X_Q} \text{ moles of solution Q} \qquad (26)$$

The amount of solution Q must be the same as the original amount since the process is cyclic. Thus the mixture having composition T and based on one mole mixture having composition R becomes

$$\left(\frac{X_T - X_S}{1 - X_S}\right)\left(\frac{1 - X_Q}{1 - X_T}\right)\left(\frac{X_R}{X_Q}\right) \text{ moles of rock} + \left(\frac{1 - X_Q}{1 - X_S}\right)\left(\frac{X_R}{X_Q}\right) \text{ moles of solution S} =$$

$$\left(\frac{X_T - X_Q}{1 - X_T}\right)\left(\frac{X_R}{X_Q}\right) \text{ moles of } CaHPO_4 + \frac{X_R}{X_Q} \text{ moles of Q solution} \qquad (27)$$

The total equation for the cycle becomes equation 25 plus 27.

$$\frac{X_Q - X_R}{X_Q} \text{ moles of } H_6(SO_4)_3 + \left(\frac{X_T - X_S}{1 - X_S}\right)\left(\frac{1 - X_Q}{1 - X_T}\right)\left(\frac{X_R}{X_Q}\right) \text{ moles of rock} +$$

$$\left(\frac{1 - X_Q}{1 - X_S}\right)\left(\frac{X_R}{X_Q}\right) \text{ moles of solution S} = \frac{X_S - X_R}{X_S} \text{ moles of } Ca_3(SO_4)_3 +$$

$$\left(\frac{X_T - X_Q}{1 - X_T}\right)\left(\frac{X_R}{X_Q}\right) \text{ moles of } CaHPO_4 + \frac{X_R}{X_S} \text{ moles of solution S} \qquad (28)$$

If the process is cyclic, the amount of S before and after the conversion must be the same:

$$\left(\frac{1 - X_Q}{1 - X_S}\right)\left(\frac{X_R}{X_Q}\right) = \frac{X_R}{X_Q} \tag{29}$$

so $X_Q = X_S$

Equation 28 then becomes

$$\frac{X_S - X_R}{X_R} \text{ moles of } H_6(SO_4)_3 + \frac{X_T - X_S}{1 - X_T} \text{ moles of phosphate rock} =$$

$$\frac{X_S - X_R}{X_R} \text{ moles of } Ca_3(SO_4)_3 + \frac{X_T - X_S}{1 - X_T} \text{ moles of } CaHPO_4 \tag{30}$$

From Figure 10

$$\frac{X_S - X_R}{X_R} = \frac{SQ}{AD} = \frac{SQ}{1} = SQ$$

$$\frac{X_T - X_S}{1 - X_T} = \frac{SQ}{FE}$$

Hence, the equation for the cycle is

$$SQ \text{ moles of } H_6(SO_4)_3 + \frac{SQ}{FE} \text{ moles of phosphate rock} =$$

$$SQ \text{ moles of } Ca_3(PO_4)_3 + \frac{SQ}{FE} \text{ moles of } CaHPO_4$$

## Rate of Reaction

When phosphate rock is added to sulfuric acid solution or phosphoric acid solution, the surface of phosphate rock is saturated with di-calcium phosphate and calcium sulfate according to the following reaction

$$Ca_3(PO_4)_2 + 2H^+ \qquad 3Ca^{++} + 2HPO_4^= \tag{31}$$

As a result of this, $H^+$ ion concentration at the surface of phosphate rock will decrease whereas the $Ca^{++}$ and the $HPO_4^=$ ion concentration will increase. In order to continue the reaction, new $H^+$ ion diffusing from the bulk solution to the surface of phosphate rock must be supplied and $Ca^{++}$ and $HPO_4^=$ ions must be removed. Di-calcium phosphate and calcium sulfate are relatively insoluble. The phosphate rock becomes covered with a layer of solid di-calcium phosphate and calcium sulfate.

In regard to the rate of the processes involved, the rate of diffusion of the $H^+$ and $Ca^{++}$ ions is the lowest. Therefore it determines the total rate of conversion.

$$\text{The rates of conversion} = V = \frac{\text{moles of disappeared } H^+}{dt}$$

$$= \frac{2 \text{ moles of } Ca^{++} \text{ dissolved}}{dt}$$

$$= \frac{2 \text{ moles of } Ca_3(PO_4)_2 \text{ converted}}{dt}$$

$$V = -\frac{dH^+}{dt} = 2\frac{d\,Ca^{++}}{dt} \tag{32}$$

The number of moles of $H^+$ ion diffusing per unit time and the number of $Ca^{++}$ ion dissolving per unit time can be calculated according to Fick's law:

$$-\frac{dH^+}{dt} = \frac{DxA}{L}\,(C_{H^+} - C^{\circ}_{H^+}) \tag{33}$$

$$\frac{dCa^{++}}{dt} = \frac{DxA}{L} \quad (C^{o}_{Ca^{++}} - C_{Ca^{++}}) \tag{34}$$

Where D is diffusing coefficient, $ft.^2/hr.$

A is surface area of the phosphate rock, $ft.^2$

L is thickness of boundary layer, ft.

$C^{o}_{H^+}$ and $C^{o}_{Ca^{++}}$ are the concentration of the $H^+$ and $Ca^{++}$ ions in the boundary layer

Since it is assumed that the diffusion determines the rate of reaction rather than chemical reaction, the reactants at the surface of the solid substance will be in equilibrium with di-calcium phosphate.

$$Ca_3(PO_4)_2 + 2H^+ \rightleftharpoons 2CaHPO_4 + Ca^{++} \tag{35}$$

$$\frac{C^{o}_{Ca^{++}}}{(C^{o}_{H^+})^2} = \text{constant}$$

or $$C^{o}_{H^+} = K\sqrt{C^{o}_{Ca^{++}}} \tag{36}$$

$C^{o}_{H^+}$ and $C^{o}_{Ca^{++}}$ can be eliminated so that V can be expressed as a function of $C_{H^+}$ and $C_{Ca^{++}}$ of the solution. In this function, the magnitudes D, A and L can be considered to be constant in a certain test or series of tests. The rate of conversion may be expressed by the following equation:

$$V^2 - \frac{DxA}{L}\left(2C_{H^+} + \frac{K^2}{2}\right)V - \left(\frac{DxA}{L}\right)^2 (K^2 C_{Ca^{++}} - C^{2}_{H^+}) = 0 \tag{37}$$

Since equation 37 is a quadratic equation, therefore V can be easily solved

$$V = \frac{DxA}{2L}\left( 2C_{H^+} + \frac{K^2}{2} \pm K\sqrt{2C_{H^+} + 4C_{Ca^{++}} + \frac{K^2}{4}}\right) \tag{38}$$

Therefore $V = f(C_{H^+}; C_{Ca^{++}})$ can be examined by partially differentiating equation 38 with respect to $C_{H^+}$ or $C_{Ca^{++}}$.

$$\left(\frac{\partial V}{\partial C_{Ca^{++}}}\right)_{C_{H^+}} = \frac{\frac{DxA}{L}\ K^2}{2\frac{L}{DxA}V - 2C_{H^+} - \frac{1}{2}K^2} \tag{39}$$

$$\left(\frac{\partial V}{\partial C_{H^+}}\right)_{C_{Ca^{++}}} = \frac{2V - 2\frac{DxA}{L}C_{H^+}}{2\frac{L}{DxA}V - 2C_{H^+} - \frac{1}{2}K^2} \tag{40}$$

From equation 33

$$V = \frac{DxA}{L}(C_{H^+} - C^{\circ}_{H^+})$$

There follows $2C_{H^+} = \frac{2L}{DxA}V + 2C^{\circ}_{H^+}$

$$2C_{H^+} > \frac{2L}{DxA}V$$

consequently the value of the denominator in 39 is negative. Therefore $\left(\frac{\partial V}{\partial C_{Ca^{++}}}\right)_{C_{H^+}}$ is negative. This means V increases as $C_{Ca^{++}}$ decrease.

In order to find the sign of $\left(\frac{\partial V}{\partial C_{H^+}}\right)_{C_{Ca^{++}}}$ the sign of

$2V - 2\frac{DxA}{L}C_{H^+}$ must be determined. From equation 33

$$V = -\frac{dH^+}{dt} = \frac{DxA}{L}(C_{H^+} - C^{\circ}_{H^+})$$

a negative value for $2V - 2 \frac{DxA}{L} C_{H^+}$ is indicated, hence the sign of $\left( \frac{\partial V}{\partial C_{H^+}} \right)_{C_{Ca^{++}}}$ is positive. The rate of conversion increases with the $C_{H^+}$ of the solution. In order to obtain a high rate of conversion the circulating liquid of the cyclic process must be satisfied by the following requirements:

1. The concentration of the $H^+$ ions of solution Q should be as high as possible.
2. The concentration of the $Ca^{++}$ ions of solution Q should be as low as possible.

## LABORATORY SCALE WORK

As a result of the equilibrium studies on the $CaO-P_2O_5-SO_3-H_2O$ system, a process was proposed for the manufacture of di-calcium phosphate. The process consists of over acidulating phosphate rock with sulfuric acid and removing $CaSO_4$ by filtration. Additional phosphate rock is added to the filtrate[1] at the boiling point producing a solid product containing di-calcium phosphate which is separated by a second filtration. The filtrate is fortified with 40% sulfuric acid and $CaSO_4$ again precipitated. This filtrate is used for subsequent conversions.

The proposed process was investigated on a laboratory scale. The variables studied were the concentration of solution S indicated in the diagram Figure 10, the acidulation ratio, the position of point T in the diagram Figure 10 and the effect of high temperature curing. One hundred grams of phosphate rock were used in each experiment.

### Raw Material

The phosphate rock used in this study was obtained from Davison Chemical Corporation plant at Perry, Iowa. The chemical composition and screen analysis are given in Table 6.

The sulfuric acid used was industrial grade purchased from Baker and Adamson Company.

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[1]The filtrate is designated as solution S

Table 6. Analysis of Florida phosphate rock (dry basis)

| Chemical constituent | | Weight percent |
|---|---|---|
| $P_2O_5$ | | 33.2 |
| CaO | | 47.8 |
| MgO | | 0.4 |
| F | | 4.2 |
| $Fe_2O_3$ | | 1.1 |
| $Al_2O_3$ | | 1.2 |
| $SiO_2$ | | 9.1 |
| Moisture | | 0.6 |
| Screen size | | |
| +65 | mesh | 0 |
| -65+100 | mesh | 2.6 |
| -100+150 | mesh | 11.0 |
| -150+200 | mesh | 24.9 |
| -200 | mesh | 61.5 |

## Analyses

All samples obtained were ground through 80 mesh and analyzed for total $P_2O_5$, water soluble $P_2O_5$, citrate insoluble $P_2O_5$, free acid and moisture. The samples were extracted for total water soluble and citrate soluble $P_2O_5$. The $P_2O_5$ content of the solution was determined colorimetrically by the method of Bridger, Boylan and Markey (8). Iron and aluminum oxide were determined according to the methods of the Association of Florida Phosphate Mining chemists. Fluorine, calcium, oxide, magnesium oxide, carbon dioxide free acid and moisture were made according to the official methods of the Association of Official Agricultural Chemists (1).

## Procedure

The laboratory experiments were carried out in a small one-liter, closed, Pyrex glass mixer mounted with three vertical condensers to reflux any escaping water vapors. The mixer was surrounded by a Glas Col heater. The general procedure consisted of:

(1) Preparing a solution S from sulfuric acid and phosphate rock with varying concentrations of free water, $m$[1]. The acidulation ratio used was 3.34 by weight or 4.83 by mole. Liquid and solid were separated by filtration. The filtrate was designated S as shown on Figure 10.

(2) Mixing phosphate rock and solution S in varing $H_6/P_2O_5$ mole ratios. This was accomplished in a Pyrex glass mixer with the wall temperature of the Pyrex glass maintained between 180-190°C. (The boiling point is about 103°C). The mixture was agitated by a stirrer inserted through a vertical condenser tube. A mixing time of about 15 minutes was used.

(3) Filtering the mixtures at the boiling temperature in a pre-heated Buchner type funnel. The solids from this filtration contained mono-calcium phosphate and di-calcium phosphate and analyzed about 40% total $P_2O_5$. If these solids were mixed with the precipitated $CaSO_4$ from step (1) for disposal, the total $P_2O_5$ analyzed about 20%.

(4) Fortifying the filtrate with 40% sulfuric acid to precipitate the calcium ion as calcium sulfate.

---

[1] m is used to design concentration of free water per two moles of $H_6(SO_4)_3$, $Ca_3(SO_4)_3$, $H_6(PO_4)_2$ and $Ca_3(PO_4)_2$ in solution

(5) Separating the precipitated $CaSO_4$ from the solution by filtration. This filtrate is again solution S.

## Results

Table 7 indicates that the concentration of solution S has a great effect on the $P_2O_5$ availability, citrate soluble[1] $P_2O_5$, and water soluble $P_2O_5$ content. These values are all decreased by increasing m values. This is shown in Figure 12. The maximum value of citrate soluble $P_2O_5$ occurs when m = 20 and the $H_6/P_2O_5$ ratio = 2.16. It can be concluded that an m value of 20 is the optimum concentration of solution S. From the filtration point of view the solution S should be as diluted as possible since it is generally more difficult to filter at high concentrations.

The position of point T shown in Figure 10 can be best represented by the ratio of FT/TS which is the mol ratio of solution S to phosphate rock added. Five ratio values, 4.5, 3.7, 3.0, 2.16, and 1.36 at m = 20 were used. The results in Table 8 show that a ratio of 2.16 gave a maximum citrate soluble $P_2O_5$ content of 33.8%. This was equivalent to 94% $P_2O_5$ availability. $P_2O_5$ availability and the total $P_2O_5$ in the solution were increased by increasing the $H_6/P_2O_5$ ratio. This is shown in Figure 13.

An important factor in any acidulation process is the consumption of acid or the total acidulation ratio. For this process five total acidulation ratios were used, 3.0, 2.6, 2.3, 2.1 and 1.6. A total

---

[1] Citrate soluble $P_2O_5$ is designated by its solubility in neutral ammonium citrate solution. Di-calcium phosphate is also soluble in the same neutral ammonium citrate solution

Table 7. Results of acidulation of phosphate rock with solution S

| Sample no. | Mol ratio $\frac{FT}{TS}$[b] | Solution T[a] m[c] | Solution T[a] Density g/c.c. | Solution T[a] Total $P_2O_5$ % | Analyses of solid product, % Total $P_2O_5$ | Water soluble $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate soluble $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|
| 1-AA | 4.5 | 10 | 1.190 | 19.9 | 48.6 | 23.7 | 0.2 | 24.7 |
| BA | 4.5 | 20 | 1.263 | 24.3 | 35.0 | 18.3 | 0.4 | 16.3 |
| CA | 4.5 | 30 | 1.196 | 20.7 | 31.2 | 15.0 | 1.5 | 14.8 |
| DA | 4.5 | 40 | 1.157 | 20.3 | 28.0 | 9.9 | 6.4 | 11.7 |
| EA | 4.5 | 50 | 1.144 | 16.0 | 27.1 | 11.5 | 3.7 | 11.9 |
| FA | 4.5 | 60 | 1.105 | 12.3 | 23.0 | 5.8 | 9.8 | 7.3 |
| GA | 4.5 | 70 | 1.107 | 11.1 | 24.0 | 6.1 | 6.5 | 11.4 |
| HA | 4.5 | 80 | 1.083 | 8.5 | 23.0 | 3.0 | 12.8 | 7.2 |
| IA | 4.5 | 90 | 1.082 | 7.6 | 23.0 | 5.0 | 7.3 | 9.7 |
| JA | 4.5 | 100 | 1.064 | 6.7 | 22.0 | 2.4 | 13.5 | 6.0 |
| 2-AA | 2.16 | 10 | 1.169 | 25.6 | 43.0 | 20.4 | 0.9 | 21.7 |
| BA | 2.16 | 20 | 1.196 | 20.1 | 41.4 | 5.4 | 2.2 | 33.8 |
| CA | 2.16 | 30 | 1.194 | 19.3 | 39.2 | 5.3 | 2.4 | 31.5 |
| DA | 2.16 | 40 | 1.177 | 19.1 | 34.8 | 7.2 | 3.8 | 23.8 |
| EA | 2.16 | 50 | 1.142 | 14.6 | 33.5 | 6.8 | 4.3 | 22.4 |
| FA | 2.16 | 60 | 1.128 | 11.8 | 33.4 | 6.3 | 4.6 | 23.5 |
| GA | 2.16 | 70 | 1.118 | 10.8 | 30.5 | 5.2 | 7.5 | 17.8 |
| HA | 2.16 | 80 | 1.105 | 10.7 | 28.8 | 5.1 | 8.9 | 14.8 |
| IA | 2.16 | 90 | 1.095 | 8.8 | 26.7 | 5.4 | 9.4 | 11.9 |
| JA | 2.16 | 100 | 1.082 | 7.1 | 26.1 | 4.9 | 10.6 | 10.6 |
| 3-BA | 1.36 | 20 | 1.145 | 14.4 | 39.5 | 14.5 | 10.2 | 14.8 |
| CA | 1.36 | 30 | 1.150 | 17.4 | 36.0 | 6.5 | 12.6 | 16.9 |
| DA | 1.36 | 40 | 1.138 | 17.1 | 34.4 | 10.3 | 13.5 | 10.6 |
| EA | 1.36 | 50 | 1.139 | 12.0 | 34.4 | 5.8 | 13.1 | 15.5 |
| FA | 1.36 | 60 | 1.148 | - | 33.3 | 8.5 | 15.2 | 9.6 |
| GA | 1.36 | 70 | 1.116 | 10.5 | 35.2 | 4.6 | 15.2 | 15.4 |
| HA | 1.36 | 80 | 1.114 | 12.9 | 32.3 | 5.0 | 15.5 | 11.3 |
| JA | 1.36 | 100 | 1.092 | 10.9 | 31.2 | 3.6 | 18.7 | 8.9 |

[a]The T point is shown on Figure 10

[b]$H_6/P_2O_5$ is the ratio of solution S to phosphate rock added or line of $\frac{FT}{TS}$ sl

[c]m is used to design concentration of free water per two moles of $H_6(SO_4)_3$, Ca

[d]Citrate soluble $P_2O_5$ = total $P_2O_5$ - water soluble $P_2O_5$ - citrate insoluble $P_2$

[e]Available $P_2O_5$ = total $P_2O_5$ - citrate insoluble $P_2O_5$

| product, % | | | Analyses solid product with $CaSO_4$ added, % | | | | | |
|---|---|---|---|---|---|---|---|---|
| Citrate soluble $P_2O_5$ | Avail. $P_2O_5$ | $P_2O_5$ Availability | Total $P_2O_5$ | Water soluble $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate[d] soluble $P_2O_5$ | Avail.[e] $P_2O_5$ | $P_2O_5$ Availability |
| 24.7 | 48.4 | 99.6 | 19.6 | 9.1 | 0.2 | 10.3 | 19.4 | 99.0 |
| 16.3 | 34.6 | 98.8 | 19.4 | 8.2 | 0.4 | 10.8 | 19.0 | 98.2 |
| 14.8 | 29.8 | 95.5 | 20.1 | 9.6 | 0.9 | 9.6 | 19.2 | 95.5 |
| 11.7 | 21.6 | 77.2 | 20.6 | 6.0 | 5.3 | 9.3 | 15.3 | 74.3 |
| 11.9 | 23.4 | 86.4 | 20.8 | 8.4 | 3.5 | 8.9 | 17.3 | 83.2 |
| 7.3 | 13.1 | 57.0 | 19.7 | 4.5 | 8.6 | 6.6 | 11.1 | 56.3 |
| 11.4 | 17.5 | 73.0 | 19.5 | 5.2 | 5.5 | 9.2 | 14.0 | 71.8 |
| 7.2 | 10.2 | 44.5 | 18.4 | 2.7 | 9.8 | 5.9 | 8.6 | 46.7 |
| 9.7 | 14.7 | 66.8 | 18.3 | 3.7 | 6.3 | 8.3 | 12.0 | 65.6 |
| 6.0 | 8.4 | 38.1 | 18.1 | 1.9 | 11.2 | 5.0 | 6.9 | 38.1 |
| 21.7 | 42.1 | 97.8 | 21.8 | 9.6 | 1.0 | 11.2 | 20.8 | 95.2 |
| 33.8 | 39.2 | 94.6 | 21.8 | 3.6 | 1.3 | 16.9 | 20.5 | 93.8 |
| 31.5 | 31.8 | 94.0 | 21.9 | 3.1 | 1.4 | 17.4 | 20.5 | 93.7 |
| 23.8 | 31.0 | 89.2 | 22.2 | 4.4 | 2.1 | 15.7 | 20.1 | 91.0 |
| 22.4 | 39.2 | 87.2 | 20.8 | 2.8 | 2.7 | 15.3 | 18.1 | 87.0 |
| 23.5 | 28.8 | 83.7 | 20.9 | 2.1 | 3.6 | 15.2 | 17.3 | 83.0 |
| 17.8 | 23.0 | 75.5 | 20.5 | 1.3 | 5.2 | 14.0 | 15.3 | 74.6 |
| 14.8 | 19.9 | 67.7 | 20.8 | 0.9 | 7.1 | 12.8 | 13.7 | 66.0 |
| 11.9 | 17.3 | 64.8 | 20.3 | 1.3 | 7.5 | 11.5 | 12.8 | 63.0 |
| 10.6 | 15.5 | 59.4 | 20.5 | 0.8 | 8.4 | 11.3 | 12.1 | 59.1 |
| 14.8 | 29.3 | 74.4 | 23.7 | 9.3 | 5.9 | 9.9 | 17.8 | 75.0 |
| 16.9 | 23.4 | 65.1 | 23.5 | 4.1 | 7.5 | 11.9 | 16.0 | 68.1 |
| 10.6 | 20.9 | 60.8 | 23.8 | 6.2 | 8.6 | 9.0 | 15.2 | 63.9 |
| 15.5 | 21.3 | 61.8 | 24.0 | 2.1 | 9.1 | 12.8 | 14.9 | 62.2 |
| 9.6 | 18.1 | 54.4 | 24.5 | 4.8 | 10.9 | 8.8 | 13.6 | 56.7 |
| 15.4 | 20.0 | 56.8 | 24.2 | 2.3 | 12.1 | 11.9 | 12.1 | 54.7 |
| 11.3 | 16.8 | 52.0 | 24.1 | 3.2 | 12.2 | 9.6 | 11.9 | 50.2 |
| 8.9 | 12.5 | 40.1 | 24.3 | 2.8 | 11.9 | 7.6 | 10.4 | 42.8 |

ıe of $\frac{\overline{FT}}{\overline{TS}}$ shown on Figure 10

$H_6(SO_4)_3$, $Ca_3(SO_4)_3$, $H_6(PO_4)_2$ and $Ca_3(PO_4)_2$ in solution

insoluble $P_2O_5$

Figure 12. Effect of the concentration of solution S on conversion at various $H_6/P_2O_5$ ratio

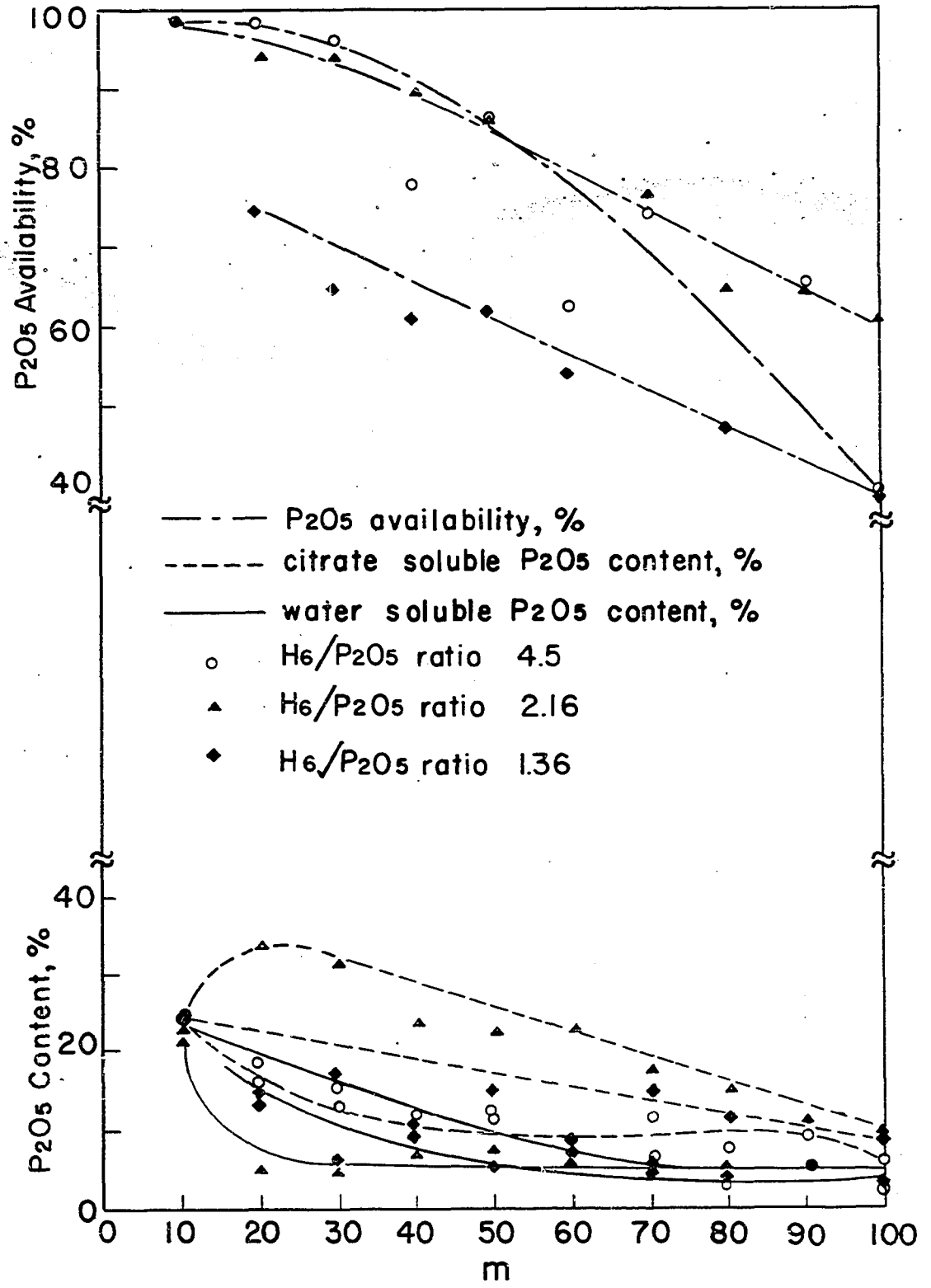

100
80
60
40
P2O5 Availability, %
P2O5 availability, %
citrate soluble P2O5 content, %
water soluble P2O5 content, %
H6/P2O5 ratio 4.5
H6/P2O5 ratio 2.16
H6/P2O5 ratio 1.36
40
20
0
P2O5 Content, %
0
10
20
30
40
50
60
70
80
90
100
m

Table 8. Results of varying $H_6/P_2O_5$ ratio

| Sample no. | $H_6/P_2O_5$ ratio | Analyses % | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Solution | Solid product | | | | | |
| | | Solution total $P_2O_5$ | Total $P_2O_5$ | Water sol. $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate sol. $P_2O_5$ | Avail. $P_2O_5$ | $P_2O_5$ availability |
| 5-A | 4.5 | 24.3 | 35.0 | 18.3 | 0.4 | 16.3 | 34.6 | 98.8 |
| 5-B | 3.7 | 24.0 | 40.1 | 14.5 | 0.8 | 24.8 | 39.3 | 98.0 |
| 5-C | 3.0 | 22.6 | 40.8 | 11.5 | 1.2 | 28.1 | 39.6 | 97.0 |
| 5-D | 2.16 | 20.1 | 41.4 | 5.4 | 2.2 | 33.8 | 39.2 | 94.6 |
| 5-E | 1.36 | 14.4 | 39.5 | 6.5 | 10.2 | 22.8 | 39.3 | 74.4 |

acidulation ratio of 2.3 gave a maximum citrate soluble $P_2O_5$ content of 33.8%. It is shown in Table 9 and Figure 14.

To investigate the effect of high temperature on curing of the product (10, 11), total acidulation ratios of 1.45, 1.55 and 1.72 were used at different curing times varying from 3 days to 21 days. Table 10 and Figure 15 show that in general high temperature curing at different total acidulation ratios has little effect on the $P_2O_5$ availability. It seems that the citrate soluble $P_2O_5$ decreases with increasing curing time at a total acidulation weight ratio of 1.72. After three days of curing no free acid could be detected in the samples.

The maximum product contained 94.6% $P_2O_5$ availability, 41.4 per cent total $P_2O_5$, 33.8% citrate soluble $P_2O_5$ and 5.4% water soluble $P_2O_5$.

In an effort to obtain maximum conversion some of the product,

Figure 13. Effect of $H_5/P_2O_5$ ratio on conversion

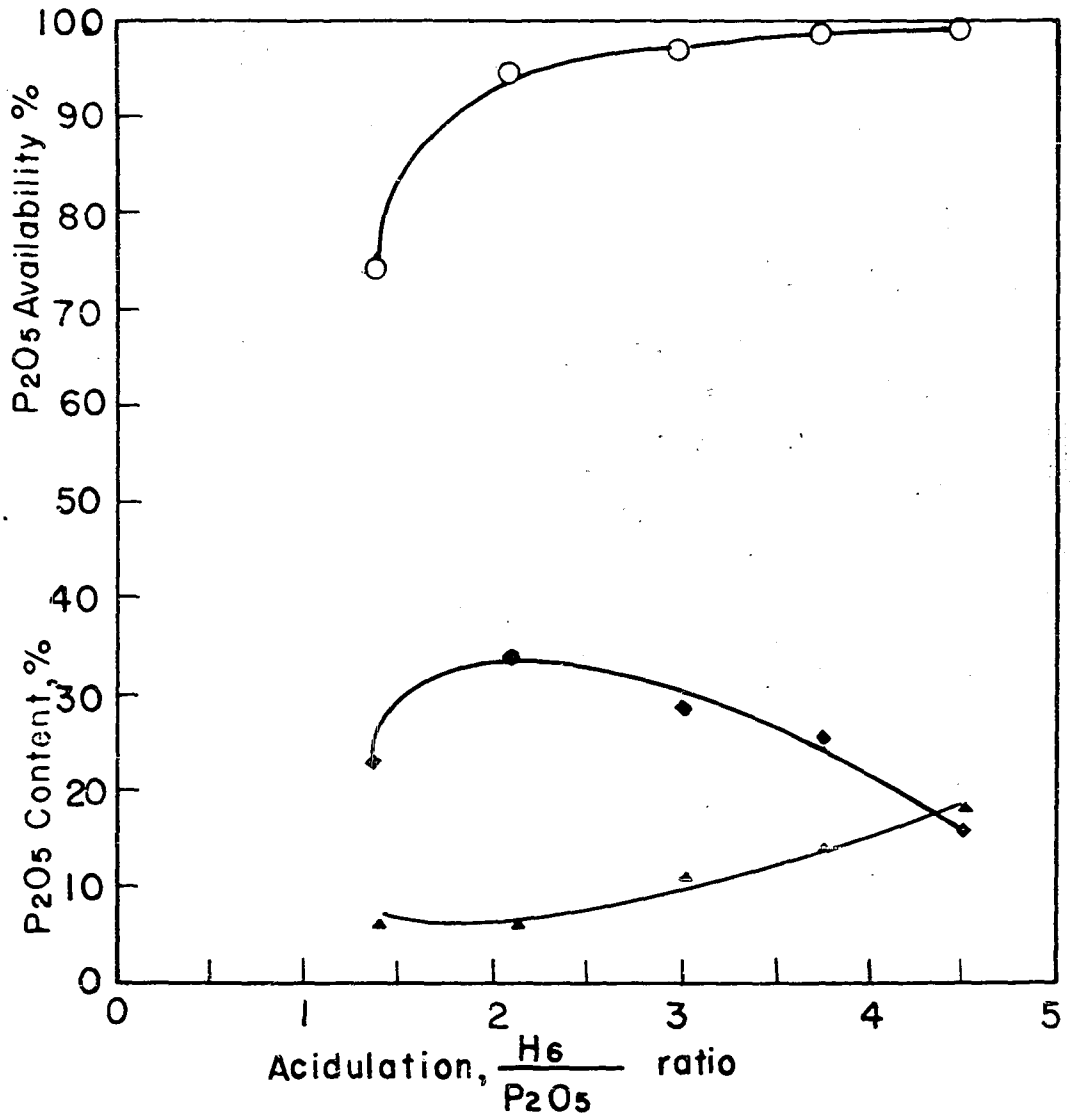

100
90
80
70
60
50
40
30
20
10
0
P2O5 Availability %
P2O5 Content, %
0
1
2
3
4
5
Acidulation, H6 / P2O5 ratio

Table 9. Results of varying total acidulation ratio

| Sample no. | Total acid ratio | $H_6/P_2O_5$ ratio | Analysis of solid product % Total $P_2O_5$ | Water sol. $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate sol. $P_2O_5$ | Avail. $P_2O_5$ | $P_2O_5$ availability |
|---|---|---|---|---|---|---|---|---|
| 6-AP | 3.0 | 2.1 | 40.5 | 26.8 | 0 | 13.7 | 40.5 | 100 |
| 6-BP | 2.6 | 2.1 | 41.2 | 16.1 | 1.0 | 24.1 | 46.2 | 97.6 |
| 6-CP | 2.3 | 2.1 | 41.6 | 5.8 | 2.6 | 33.2 | 39.0 | 93.8 |
| 6-DP | 2.0 | 2.1 | 40.6 | 9.0 | 4.3 | 29.3 | 36.3 | 88.9 |
| 6-EP | 1.6 | 2.1 | 40.9 | 7.8 | 20.2 | 12.9 | 20.7 | 51.0 |

which contained a small amount of undecomposed phosphate rock, was mixed with the precipitated $CaSO_4$ from the first filtration for approximately 15 minutes at 180°C (33). The purpose of this step was to convert the undecomposed phosphate rock by allowing it to react with acid adhering to the $CaSO_4$. The results are shown in Table 7. The available $P_2O_5$ and citrate soluble $P_2O_5$ did not change but the total $P_2O_5$ was decreased by dilution with the $CaSO_4$ to 20%. The total acidulation ratio was still 2.3 moles per cycle. Therefore it is concluded that the only benefit of $CaSO_4$ addition might be to dispose of the gypsum by-product.

Figure 14. Effect of total acidulation ratio on conversion

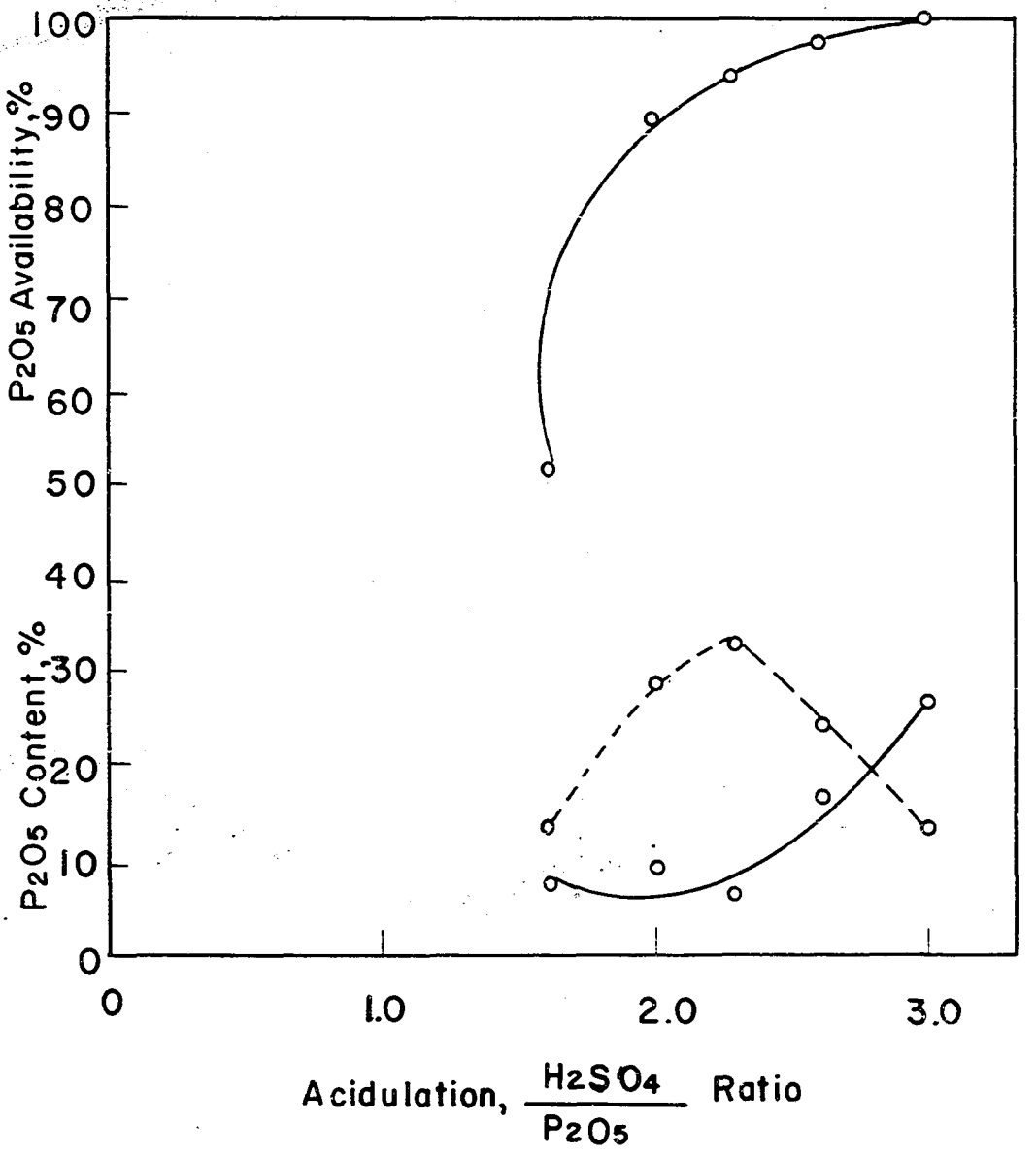
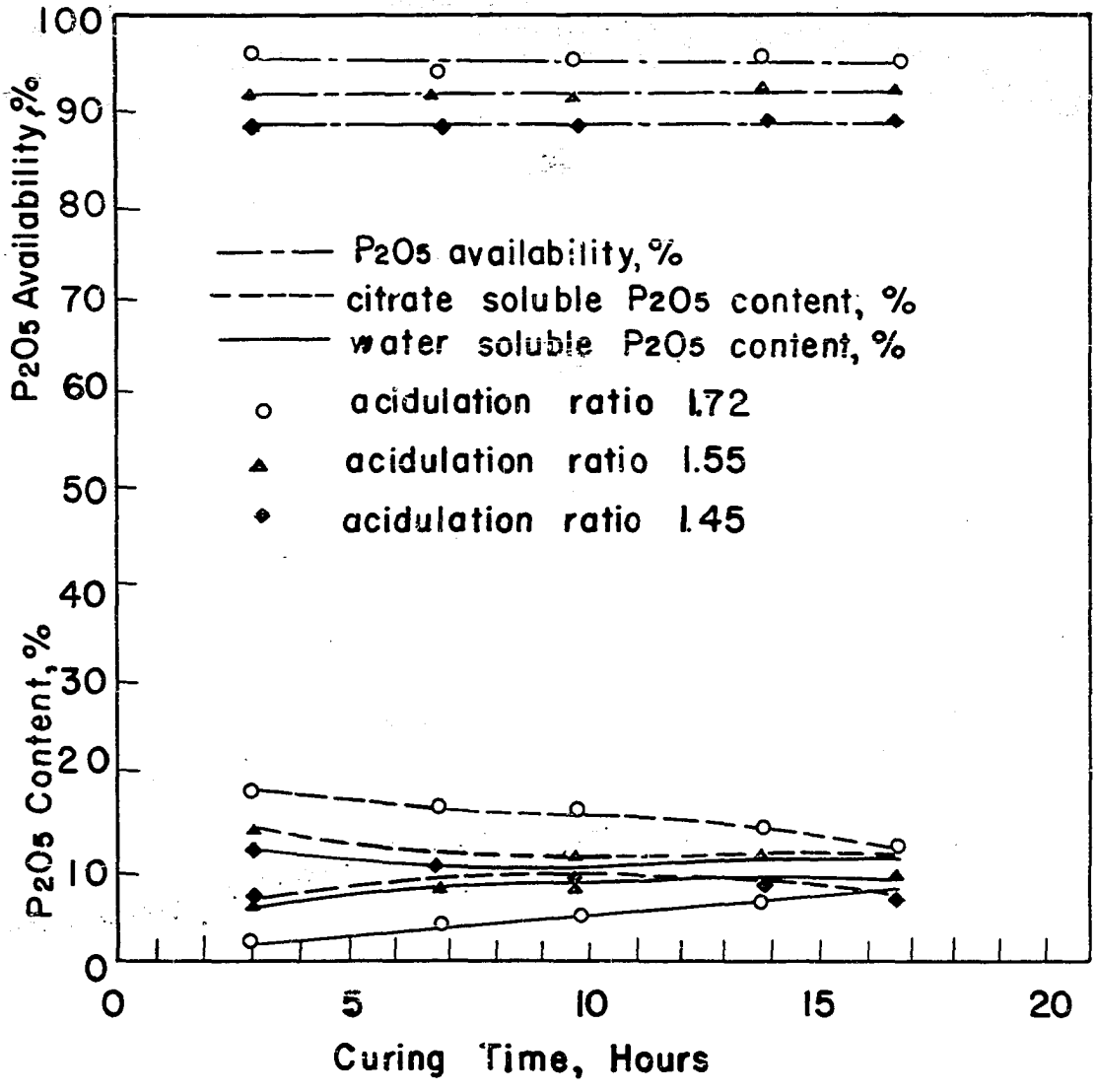

100
90
80
70
60
50
40
30
20
10
0
P2O5 Availability,%
P2O5 Content,%
0
1.0
2.0
3.0
Acidulation, H2SO4 / P2O5 Ratio

Table 10. Results of high temperature curing

| Sample no. | Curing temp. °F | Acidulation ratio $\frac{H_2SO_4}{P_2O_5}$ | Curing time (day) | Analysis of product % | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Total $P_2O_5$ | Water sol. $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate sol. $P_2O_5$ | Avail. $P_2O_5$ | Free acid | $P_2O_5$ availability |
| F9a | 293 | 1.45 | 3 | 21.9 | 12.2 | 2.5 | 7.2 | 19.4 | 0 | 88.5 |
| F9b | 293 | 1.45 | 7 | 22.8 | 10.5 | 2.7 | 9.6 | 20.1 | 0 | 88.2 |
| F9c | 293 | 1.45 | 10 | 24.0 | 11.4 | 2.8 | 9.8 | 21.2 | 0 | 88.4 |
| F9d | 293 | 1.45 | 14 | 22.3 | 11.2 | 2.7 | 8.4 | 19.6 | 0 | 88.0 |
| F9e | 293 | 1.45 | 17 | 21.9 | 11.0 | 2.4 | 8.5 | 19.5 | 0 | 89.0 |
| F9f | 293 | 1.45 | 21 | 24.0 | 9.0 | 2.5 | 13.5 | 21.5 | 0 | 89.5 |
| $F9A_3$ | 293 | 1.55 | 3 | 22.6 | 6.7 | 1.8 | 14.1 | 20.8 | 0 | 92.0 |
| $F9B_3$ | 293 | 1.55 | 7 | 21.9 | 8.0 | 1.7 | 12.2 | 20.2 | 0 | 92.2 |
| $F9C_3$ | 293 | 1.55 | 10 | 21.8 | 8.4 | 2.0 | 11.4 | 19.8 | 0 | 91.0 |
| $F9D_3$ | 293 | 1.55 | 14 | 22.8 | 9.0 | 1.7 | 12.1 | 21.1 | 0 | 92.6 |
| $F9E_3$ | 293 | 1.55 | 17 | 23.4 | 9.3 | 1.8 | 12.3 | 21.6 | 0 | 92.5 |
| $F9F_3$ | 293 | 1.55 | 21 | 23.5 | 8.6 | 1.8 | 13.1 | 21.7 | 0 | 92.6 |
| F9A | 293 | 1.72 | 3 | 22.8 | 3.4 | 0.9 | 18.5 | 21.9 | 0 | 96.0 |
| F9B | 293 | 1.72 | 7 | 22.0 | 4.5 | 1.2 | 16.7 | 21.1 | 0 | 94.0 |
| F9C | 293 | 1.72 | 10 | 22.4 | 5.0 | 1.1 | 16.3 | 21.3 | 0 | 95.4 |
| F9D | 293 | 1.72 | 14 | 21.9 | 7.1 | 0.9 | 14.1 | 21.0 | 0 | 96.0 |
| F9E | 293 | 1.72 | 17 | 21.3 | 8.0 | 1.0 | 12.0 | 20.3 | 0 | 95.3 |
| F9F | 293 | 1.72 | 21 | 21.7 | 7.0 | 1.1 | 13.6 | 20.6 | 0 | 95.0 |

Figure 15. Effect of curing time on conversion at various curing temperature


100
90
80
70
60
50
40
30
20
10
0
P2O5 Availability,%
P2O5 Content, %
0
5
10
15
20
Curing Time, Hours
P2O5 availability, %
citrate soluble P2O5 content, %
water soluble P2O5 content, %
acidulation ratio 1.72
acidulation ratio 1.55
acidulation ratio 1.45

# PILOT PLANT WORK

## Description of Equipment

The pilot plant originally built by Kaufman (26) was modified for this work. It consisted of a vibrating feeder, a continuous mixer, four settling tanks and two steam-jacketed paddle conveyors. The conveyors were connected in series, one above the other and were driven by a motor and gear reducer as shown in Figure 16.

The continuous mixer consisted of an inverted truncated cone with a cylindrical extension attached to the bottom of the cone. Acid and rock were introduced into an open cylindrical can supported inside the cone. A stirrer was placed in the can and the acid mix overflowed continuously. Details of the continuous mixer are shown in Figure 17.

Each conveyor consisted of a series of paddles mounted on a 3/4 inch diameter shaft inside a 60 inch section of 3 inch diameter pipe. This 3 inch pipe was surrounded by a 48 inch section of 6 inch steel pipe jacket. The paddles were angled at 45 degrees to convey the mixture forwarded. High pressure steam (80 to 90 psig) was used in the 6 inch steel pipe jacket.

Two settling tanks were lined with lead and the two others were made of ceramic material. All piping for acid solutions was Tygon tubing protected with thin wall conduit.

## Procedures

One hundred mesh phosphate rock and 40 percent sulfuric acid were mixed in a settling tank in an acidulation ratio of 4.83. The mix was

Figure 16. Details of the continuous mixer

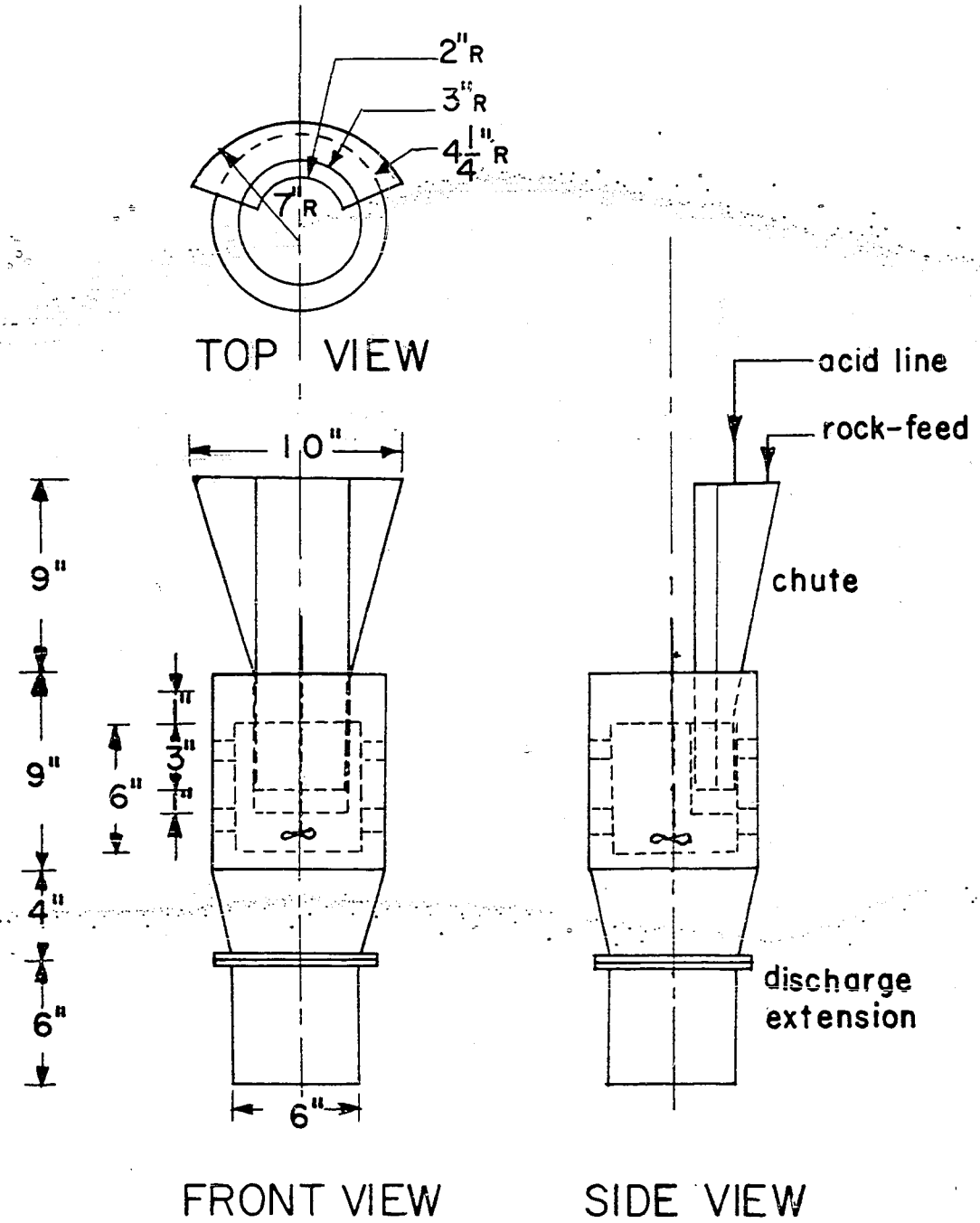
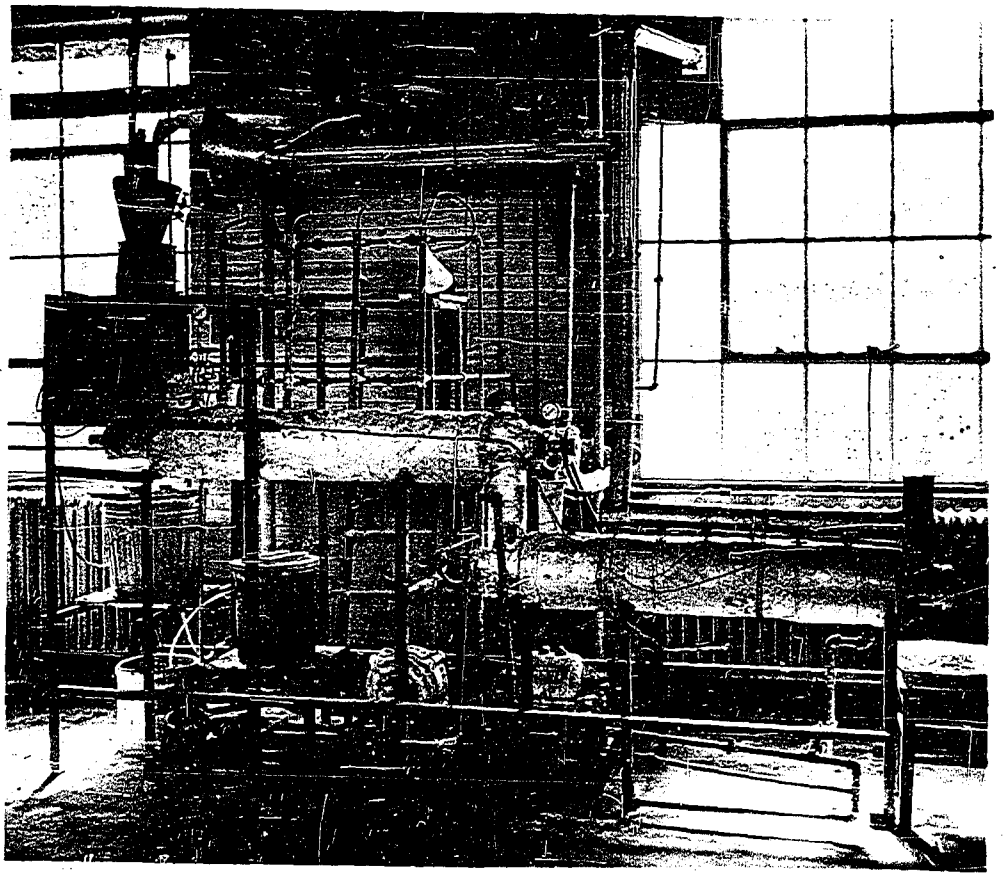

2"R
3"R
4 1/4"R
7"R
TOP VIEW
10"
9"
9"
4"
6"
6"
3"
6"
FRONT VIEW
acid line
rock-feed
chute
discharge
extension
SIDE VIEW

Figure 17. Photograph of pilot plant



allowed to remain in the tank 24 hours. The supernatant acid solution flowed to the storage tank by gravity. It was then introduced to process by means of a stainless steel pump.

Phosphate rock was fed with a vibrating feeder and was mixed with the acid solution from the settling tank in an acidulation mole ratio of 1.0.

The material passed through the first and second conveyor essentially in granular form. The steam pressure in the jacket of each conveyor was about 80 psig and a temperature of about 165°C. was measured inside the conveyor by thermocouples. Exhaust vapor from the continuous mixer and the conveyors was removed by an air jet and discharged from the building.

Analyses of the product are shown in Table 11. The product was subsequently mixed with the previously settled gypsum in the continuous mixer. The resulting product analyses are shown in Table 12.

In Table 13, analyses are given for product resulting from mixing the precipitated calcium sulfate in the second conveyor with the product from first conveyor which contained 40 percent total $P_2O_5$.

## Results

A total of nine runs were made, the first five runs were made for the purpose of developing an operating technique and eliminating mechanical trouble.

The continuous mixer performed satisfactorily except for occasional plugging at the bottom. The first conveyor did not operate satisfactorily after extended, ten hours or more, runs. The material tended to solidify

Table 11. Result of pilot plant runs

| Run and sample no. | Temp. °C. | Sample[a] time, hr. | $H_6/P_2O_5$[b] ratio | Product analysis, % by weight: Total $P_2O_5$ | Water soluble $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate[c] sol. $P_2O_5$ | Avail.[d] $P_2O_5$ | Moist. | Free acid | $P_2O_5$ availability |
|---|---|---|---|---|---|---|---|---|---|---|---|
| R6-A | 150 | 2 | 1.0 | 42.2 | 19.2 | 7.2 | 15.8 | 35.0 | 20.7 | 6.6 | 83.0 |
| R6-B | 150 | 3 | 1.0 | 43.2 | 21.1 | 6.9 | 15.2 | 36.3 | 13.3 | - | 84.2 |
| R6-C | 150 | 4 | 1.0 | 45.0 | 23.2 | 6.5 | 15.3 | 38.3 | 20.5 | 6.4 | 85.5 |
| R6-D | 150 | 5 | 1.0 | 39.3 | 23.5 | 5.8 | 10.0 | 33.5 | 19.5 | 7.5 | 85.3 |
| R6-E | 150 | 6 | 1.0 | 40.2 | 27.3 | 2.0 | 21.0 | 38.3 | 16.7 | 3.1 | 95.1 |
| R3-A | 175 | 2 | 1.2 | 41.2 | 27.3 | 4.3 | 9.6 | 36.9 | 22.0 | 5.2 | 89.2 |
| R3-B | 175 | 3 | 1.2 | 39.2 | 25.7 | 4.0 | 9.5 | 35.2 | 18.6 | 5.3 | 89.7 |
| R3-C | 175 | 4 | 1.2 | 42.1 | 27.4 | 5.0 | 9.7 | 37.1 | 20.2 | 5.1 | 88.1 |
| R3-D | 175 | 5 | 1.2 | 40.2 | 27.4 | 4.4 | 8.4 | 35.8 | 20.9 | 4.4 | 89.0 |
| R3-E | 175 | 6 | 1.2 | 43.8 | 26.5 | 5.2 | 12.1 | 38.6 | 21.4 | 4.2 | 88.2 |
| R3-F | 175 | 7 | 1.2 | 42.2 | 27.0 | 4.9 | 10.4 | 37.3 | 17.9 | 4.2 | 88.5 |
| R3-G | 175 | 8 | 1.2 | 41.2 | 28.9 | 5.0 | 7.3 | 36.2 | 16.2 | 3.4 | 87.8 |
| R3-H | 175 | 9 | 1.2 | 40.8 | 25.1 | 4.3 | 11.4 | 36.5 | 10.7 | - | 89.5 |

[a]Elapsed time between start up and sample collection

[b]$H_6/P_2O_5$ is the ratio of solution S to the phosphate rock added or line of $\frac{FT}{TS}$ shown on Figure 10

[c]Citrate soluble $P_2O_5$ = total $P_2O_5$ - water soluble $P_2O_5$ - citrate insoluble $P_2O_5$

[d]Available $P_2O_5$ = total $P_2O_5$ - citrate insoluble $P_2O_5$

Table 12. Result of mixing by product gypsum in pilot plant runs

| Run and sample no. | Temp. °C. | Sample[a] time, hr. | $H_6/P_2O_5$[b] ratio | Product analysis, % Total $P_2O_5$ | Water soluble $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate[c] sol. $P_2O_5$ | Avail.[d] $P_2O_5$ | Moist. | Free acid | $P_2O_5$ availability |
|---|---|---|---|---|---|---|---|---|---|---|---|
| R12-A | 165 | 2 | 1.0 | 19.4 | 11.6 | 2.47 | 5.3 | 16.9 | 7.9 | 0 | 87.3 |
| R12-C | 165 | 3 | 1.0 | 20.4 | 14.8 | 2.11 | 3.5 | 18.3 | 6.0 | 0 | 90.1 |
| R12-E | 165 | 4 | 1.0 | 21.7 | 14.3 | 1.69 | 6.0 | 20.1 | 5.8 | 0.72 | 92.2 |
| R12-G | 165 | 5 | 1.0 | 22.0 | 15.2 | 1.66 | 5.1 | 20.3 | 5.4 | 0.88 | 92.5 |
| R12-I | 165 | 6 | 1.0 | 21.0 | 15.4 | 2.00 | 3.0 | 19.0 | 5.5 | 0 | 90.5 |
| R2-AH | 175 | 2 | 1.2 | 19.0 | 15.4 | 0.49 | 3.1 | 18.5 | 8.6 | 3.48 | 97.4 |
| R2-BA | 175 | 3 | 1.2 | 20.3 | 16.2 | 1.07 | 3.0 | 19.2 | 7.9 | 2.28 | 94.7 |
| R2-CA | 175 | 4 | 1.2 | 20.0 | 16.0 | 1.22 | 2.8 | 18.8 | 8.1 | 2.12 | 93.9 |
| R2-DA | 175 | 5 | 1.2 | 20.0 | 16.2 | 1.39 | 2.4 | 18.6 | 8.6 | 1.96 | 93.0 |
| R2-EA | 175 | 6 | 1.2 | 20.2 | 14.1 | 0.34 | 5.8 | 19.9 | 7.6 | 3.36 | 98.7 |
| R2-FA | 175 | 7 | 1.2 | 19.7 | 15.4 | 0.76 | 3.5 | 18.9 | 7.2 | 3.04 | 96.1 |
| R2-GA | 175 | 8 | 1.2 | 19.6 | 15.5 | 0.79 | 3.3 | 18.8 | 7.2 | 3.04 | 96.0 |
| R2-HA | 175 | 9 | 1.2 | 19.7 | 15.8 | 0.55 | 3.6 | 19.1 | 7.0 | 2.75 | 97.2 |

[a]Elapsed time between start up and sample collection

[b]$H_6/P_2O_5$ is the ratio of solution S to the phosphate rock added or line of $\frac{\overline{FT}}{\overline{TS}}$ shown on Figure 10

[c]Citrate soluble $P_2O_5$ = total $P_2O_5$ - water soluble $P_2O_5$ - citrate insoluble $P_2O_5$

[d]Available $P_2O_5$ = total $P_2O_5$ - citrate insoluble $P_2O_5$

Table 13. Result of mixing by product gypsum in second conveyor of pilot plant

| Run and sample no. | Temp. °C. | Sample[a] time, hr. | $\frac{H_2SO_4}{P_2O_5}$ ratio by weight | Product analysis, % by weight | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Total $P_2O_5$ | Water soluble $P_2O_5$ | Citrate insol. $P_2O_5$ | Citrate[b] sol. $P_2O_5$ | Avail.[c] $P_2O_5$ | Moist. | Free acid | $P_2O_5$ availability |
| R2-A | 175 | 2 | 1.58 | 19.8 | 16.3 | 2.1 | 1.4 | 17.7 | 14.7 | 4.6 | 89.4 |
| R2-B | 175 | 3 | 1.58 | 19.8 | 16.3 | 2.0 | 1.5 | 17.8 | 8.3 | 4.0 | 89.7 |
| R2-C | 175 | 4 | 1.58 | 19.3 | 16.4 | 2.2 | 0.7 | 17.1 | 6.9 | 5.2 | 88.6 |
| R2-D | 175 | 5 | 1.58 | 20.5 | 16.3 | 2.2 | 2.0 | 18.3 | 6.7 | 5.0 | 89.2 |
| R2-E | 175 | 6 | 1.58 | 19.8 | 15.0 | 1.4 | 3.4 | 18.4 | 8.6 | 6.2 | 92.8 |
| R2-F | 175 | 7 | 1.58 | 19.8 | 15.0 | 1.9 | 2.9 | 17.9 | 7.5 | 4.8 | 90.5 |
| R2-G | 175 | 8 | 1.58 | 19.3 | 15.8 | 1.6 | 1.9 | 17.7 | 9.5 | 5.0 | 91.7 |
| R2-H | 175 | 9 | 1.58 | 19.8 | 16.2 | 1.5 | 2.1 | 17.3 | 8.5 | 4.8 | 92.5 |
| R2-I | 175 | 10 | 1.58 | 19.8 | 16.4 | 1.4 | 2.0 | 18.4 | 8.7 | 4.6 | 93.1 |
| R2-J | 175 | 11 | 1.58 | 19.3 | 16.3 | 1.4 | 1.6 | 17.9 | 8.7 | 4.5 | 92.5 |
| R2-A | 175 | 2 | 1.8 | 19.8 | 16.0 | 1.2 | 2.6 | 18.6 | 9.9 | 4.2 | 94.0 |
| R7-B | 175 | 3 | 1.8 | 18.0 | 13.0 | 1.3 | 3.8 | 16.7 | 7.4 | 2.7 | 93.0 |
| R7-C | 175 | 4 | 1.8 | 18.0 | 12.3 | 2.2 | 3.5 | 15.8 | 9.6 | 1.5 | 88.0 |
| R7-D | 175 | 5 | 1.8 | 18.0 | 14.2 | 1.1 | 2.7 | 16.9 | 6.1 | 4.4 | 94.0 |
| R7-E | 175 | 6 | 1.8 | 18.1 | 15.9 | 0.7 | 1.4 | 17.4 | 6.0 | 5.7 | 96.0 |
| R7-F | 175 | 7 | 1.8 | 19.3 | 15.9 | 0.4 | 3.0 | 18.9 | 6.7 | 6.4 | 98.1 |
| R7-G | 175 | 8 | 1.8 | 18.1 | 15.9 | 0.3 | 2.9 | 17.8 | 6.6 | 6.5 | 98.1 |
| R7-H | 175 | 9 | 1.8 | 19.2 | 15.8 | 0.6 | 2.8 | 18.6 | 5.8 | 3.9 | 97.0 |
| R7-I | 175 | 10 | 1.8 | 19.2 | 15.9 | 0.5 | 2.8 | 18.7 | 5.6 | 5.6 | 97.6 |

[a]Elapsed time between start up and sample collection

[b]Citrate soluble $P_2O_5$ = total $P_2O_5$ - water soluble $P_2O_5$ - citrate insoluble $P_2O_5$

[c]Available $P_2O_5$ = total $P_2O_5$ - citrate insoluble $P_2O_5$

in this conveyor and to freeze the paddle shaft. In these instances, it was necessary to flush the conveyor with water. The temperatures inside the first and second conveyor were changed from 175°C. to 165°C. or 150°C. at $H_6/P_2O_5$ acidulation ratio = 1.0, because the material tended to solidify in the first conveyor.

It was found that after two to three hours of operation, a steady state could be reached, which was indicated by a constant product rate and constant $P_2O_5$ availability.

The $H_6/P_2O_5$ ratio of acid solution to rock was 1.0. The $H_2SO_4/P_2O_5$ ratio of phosphate rock to total acid used was 2.3 by mole or 1.57 by weight. A product averaging 40 percent total $P_2O_5$ having 89 percent $P_2O_5$ availability was obtained and a product averaging 22 percent total $P_2O_5$ having 92 percent $P_2O_5$ availability was obtained after precipitated calcium sulfate was added.

By using a total acidulation ratio of 1.8 by weight, a product averaging 41 percent total $P_2O_5$ and 89 percent $P_2O_5$ availability before mixing calcium sulfate and 20 percent total $P_2O_5$ and 96 percent $P_2O_5$ availability after mixing calcium sulfate was obtained.

## PROPOSED PROCESS

As a result of the pilot plant work, an industrial process for the manufacture of fertilizer grade di-calcium phosphate by direct acidulation of phosphate rock is proposed as shown in Figure 18. The product would be either 0-40-0 or 0-22-0 depending on the disposition of the by product $CaSO_4$.

In this process ground phosphate rock would be unloaded from hopper cars, stored in silos, and metered to process by a belt or vibrating feeder.

Sulfuric acid, 66°Be', would be delivered in tank cars and stored in steel tanks. It would be pumped to process and metered by a rotameter.

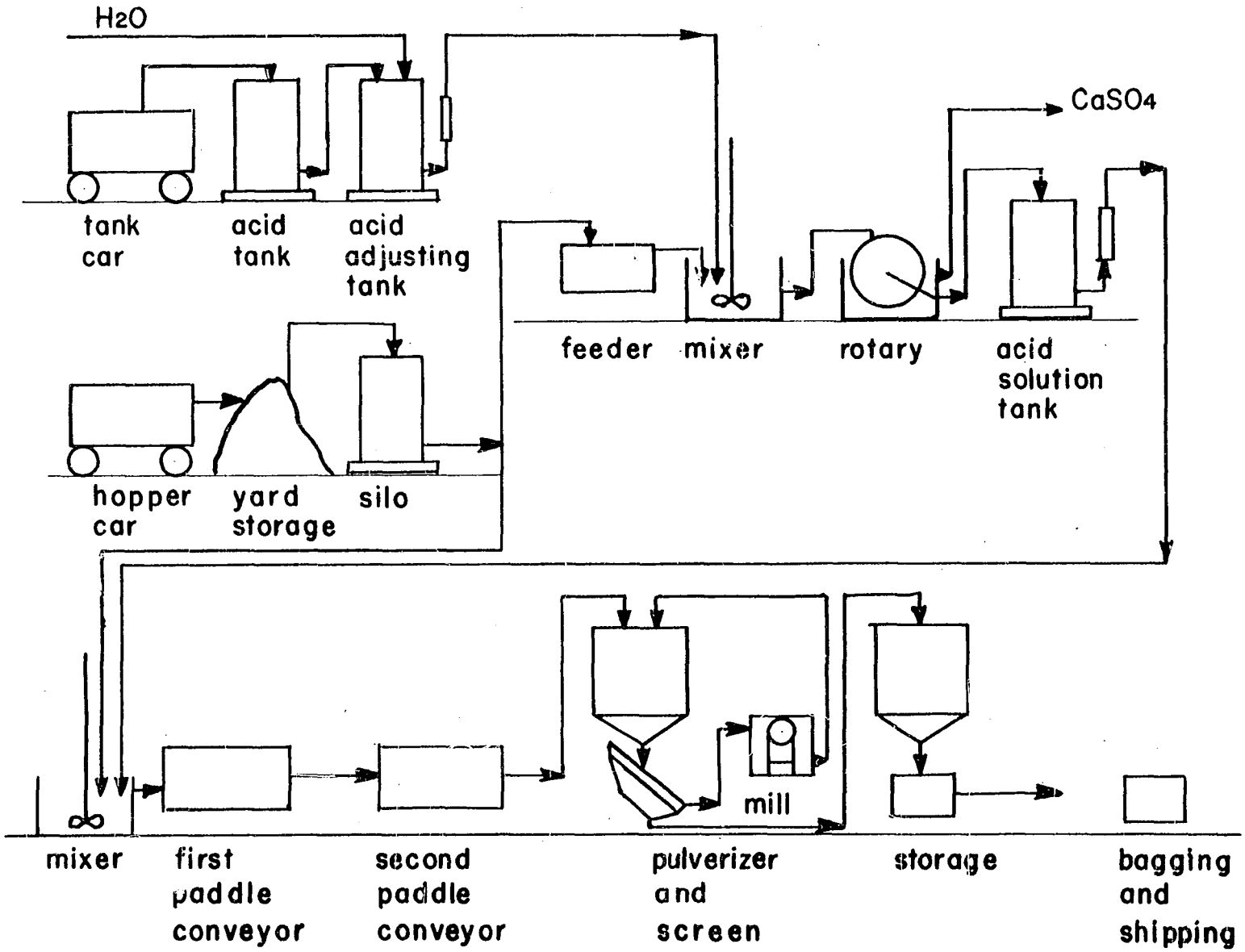
The rock and acid would be reacted in an agitated tank to produce a phosphoric acid solution and a solid by product of $CaSO_4$. The precipitated $CaSO_4$ and impurities would be separated from the acid solution by a rotary vacuum or other convenient filter.

Additional phosphate rock would then be added to the filtrate from the $CaSO_4$ separation in a second mixer and subsequently reacted in a series of paddle conveyors. The product from the last conveyor would be finished grade, 0-40-0, requiring no curing would be screened, stored and packaged.

The precipitated calcium sulfate from the first acidulation could be mixed with the solids from the first conveyor, if desired, to produce a product containing 22 percent $P_2O_5$ is gramular form.

The advantages of this process are:

Figure 18. Proposed flow sheet for a di-calcium phosphate fertilizer plant


H2O
CaSO4
tank car
acid tank
acid adjusting tank
feeder
mixer
rotary
acid solution tank
hopper car
yard storage
silo
mixer
first paddle conveyor
second paddle conveyor
mill
pulverizer and screen
storage
bagging and shipping

(a) A considerable saving in the consumption of sulfuric acid over that required to produce mono-calcium phosphate in the normal superphosphate processes. (In this process 2.3 moles of sulfuric acid are required per mole of $P_2O_5$ or 1.57 pounds of sulfuric acid per pound of $P_2O_5$. The normal superphosphate process requires 2.6 moles of sulfuric acid per mol of $P_2O_5$ or 1.8 pounds of sulfuric acid per pound of $P_2O_5$).

(b) The product requires no further curing and can be bagged and shipped directly from the process. (This reduces the required storage facilities and working capital tied up in inventory).

(c) The process can be operated on a continuous basis and can produce a granular product.

## Economic Evaluation

Tables 14 and 15 give the estimated capital investment required and the production cost for a conventional normal superphosphate plant and for the proposed di-calcium phosphate plant. The capital investment required for a plant of this size is estimated at $1,360,000, about 13 percent greater than a normal superphosphate plant.

As indicated in Table 15, the estimated manufacturing cost of normal superphosphate and di-calcium phosphate by the proposed process is $27.11 and $26.39 respectively.

The working capital, net profit and return on investment are estimated in Table 16 for a normal superphosphate and the proposed di-calcium phosphate process. Since the proposed di-calcium phosphate process requires no curing, less working capital is required. The percent return on investment for normal superphosphate and the proposed di-calcium

Table 14. Fixed capital cost estimates for a normal superphosphate and the proposed di-calcium phosphate process plants

Basis: Capacity - 120,000 short tons/year
Location - Ames, Iowa

| Item | Installed cost, dollars[a] | |
|---|---|---|
| | Normal superphosphate | Proposed di-calcium phosphate |
| Land and railroad siding | $ 20,900 | $ 20,900 |
| Process building | 103,400 | 98,500 |
| Materials handling and storage facilities | 452,000 | 237,400 |
| Major grinding equipment | 67,700 | 67,700 |
| Acid mixing and dilution equipment and dens | 73,500 | 282,000 |
| Conveyor | - | 115,000 |
| Bagging equipment | 56,500[b] | 56,500 |
| Contingencies, 20% | 156,000 | 175,600 |
| Total installed equipment | $ 930,000 | $ 1,054,000 |
| Plus insurance and taxes 2% | 18,000 | 21,100 |
| Plus contractor profit 10% | 94,860 | 107,510 |
| Plus construction overhead 15% | 156,540 | 177,390 |
| Total fixed capital investment | $1,200,000 | $ 1,360,000 |

[a]The equipment costs for the normal superphosphate plant are taken from Rounsley (43), adjusted for 1959 costs

[b]Includes superphosphate grinding equipment

phosphate are indicated as 9.0 percent and 11.6 percent respectively.

Table 15. Production cost estimates for normal superphosphate and the proposed di-calcium phosphate

Basis: 20 tons/hour, 250 days/year Location: Ames, Iowa

| Item | Unit cost[b] | Normal superphosphate[a] Quantity/ton | Normal superphosphate[a] Cost/ton | Proposed di-calcium phosphates Quantity/ton | Proposed di-calcium phosphates Cost/ton |
|---|---|---|---|---|---|
| Raw material | | | | | |
| Acid | $25.00/T | 0.371 T | $9.28 | 0.308 T | $7.70 |
| Rock | 15.0904/T | 0.594 T | 8.96 | 0.594 T | 8.96 |
| Water | 0.04/T | 0.341 T | 0.01 | 0.460 T | 0.02 |
| | | | $18.25 | | $16.68 |
| Labor | | | | | |
| Unskilled | 1.60/hr. | 0.150 man-hr. | $ 0.24 | 0.150 man-hr. | $ 0.24 |
| Semiskilled | 2.10/hr. | 0.150 man-hr. | 0.32 | 0.190 man-hr. | 0.40 |
| Skilled | 2.50/hr. | 0.100 man-hr. | 0.25 | 0.150 man-hr. | 0.38 |
| Supervision | 3.00/hr. | 0.0167 man-hr. | 0.05 | 0.0324 man-hr. | 0.10 |
| Reserve | 20% of above | | 0.16 | | 0.19 |
| | | | $ 1.02 | | $ 1.31 |
| Services | | | | | |
| Power | 0.02/kw.-hr. | 20.83 kw.-hr. | $ 0.42 | | $ 0.42 |
| Heat | 0.000 467/100 btu | | 0.00 | 200,000 btu | 0.10 |
| Water | 0.03/1000 gal. | 208 gal. | 0.01 | 500 gal. | 0.02 |
| Maintenance including labor | 20%/yr. of fixed capital | | 2.40 | | 2.26 |
| Packaging | 0.15/bag | | 3.60 | | 3.60 |
| Indirect costs | | | | | |
| Depreciation | 10%/yr. of fixed capital | | 1.00 | | 1.13 |
| Taxes and ins. | 3%/yr. of fixed capital | | 0.30 | | 0.33 |
| Overhead | 50% of labor | | 0.51 | | 0.54 |
| Total production cost | | | $27.11 | | $26.39 |

[a]The manufacturing costs for the normal superphosphate plant are taken from Rounsley (43)

[b]The unit cost and freight cost for sulfuric acid and phosphate rock are taken from Chemical Engineering News June 29, 1959

Table 16. Comparison of estimated return on investment for a normal superphosphate plant and the proposed di-calcium phosphate plant

Basis: Capacity - 20 tons/hour, 250 days/year
Location - Ames, Iowa

| Item | Normal superphosphate | | Di-calcium phosphate | |
|---|---|---|---|---|
| | Cost/ton | Amount | Cost/ton | Amount |
| Annual sales[a] | $32.34[b] | $3,880,800 | $32.34[b] | $3,880,800 |
| Manufacturing cost | | 3,253,200 | | 3,166,800 |
| Gross profit | | 627,600 | | 714,000 |
| Administration and selling cost at 3% of annual sales | | 116,400 | | 116,400 |
| Net profit, before taxes | | 511,200 | | 597,600 |
| Taxes, 50 percent | | 255,600 | | 299,800 |
| Net profit, after taxes | | 255,600 | | 299,800 |
| Working capital | | | | |
| Raw material inventory | | | | |
| Acid, 10 days | | $ 62,500 | | $ 62,500 |
| Rock, 2 weeks | | 60,300 | | 60,300 |
| In process inventory | | 427,000[c] | | 3,000 |
| Product inventory | | 199,200 | | 199,000 |
| Production for 30 days | | 429,000 | | 427,000 |
| Credit, 30 days | | 465,500 | | 465,000 |
| Total working capital | | $1,641,500 | | $1,216,800 |
| Fixed capital | | $1,200,000 | | $1,360,000 |
| Total fixed plus working capital | | $2,841,500 | | $2,576,800 |
| Percent return on investment | | 9.0 | | 11.6 |

[a]120,000 tons of 20 percent normal superphosphate are equal to 60,000 tons of 40 percent di-calcium phosphate

[b]Based on current dealer's price in Des Moines, Iowa

[c]Based on 30 days storage

# CONCLUSIONS

(1) The phase relationships of the system $CaO-P_2O_5-SO_3-H_2O$ at 100°C. and 145°C. were studied. A graphical method of representing the $CaO-P_2O_5-SO_3-H_2O$ system was developed. As the concentration of $P_2O_5$ in solution increased, the solubility of $CaSO_4$ in the solution became negligible. By using this diagram a process was proposed for the manufacture of di-calcium phosphate by direct acidulation of phosphate rock. In this process phosphate rock and 40 percent sulfuric acid are reacted and the calcium sulfate separated by filtration. Additional phosphate rock is added to the filtrate and allowed to react. The solids containing di-calcium phosphate, mono-calcium phosphate and small amount of unreacted phosphate rock were separated as product. Forty percent sulfuric acid is added to the filtrate and calcium sulfate again removed. The filtrate is then available for a new cycle.

(2) A laboratory scale study showed that the process gave a product averaging 40 percent total $P_2O_5$ and 93 percent $P_2O_5$ availability at a total acidulation ratio of 1.58 by weight. A product low in free acid and moisture was obtained. Total $P_2O_5$ in the product was reduced to 22 percent if the precipitated calcium sulfate was remixed.

(3) The process was demonstrated on the pilot plant scale omitting the second filtration step by addition of more rock and use of a paddle conveyor as a converter. The pilot plant equipment performed satisfactorily. However, some conveyor difficulty occurred after long runs. The ratio of phosphate rock to total acid used was 2.3 by mole or 1.58 by weight. A dried product having 40 percent total $P_2O_5$, 89 percent $P_2O_5$

availability and low free acid was obtained. Total $P_2O_5$ was changed to 22 percent and the $P_2O_5$ availability to 92 percent if the precipitated calcium sulfate was remixed.

(4) The proposed process appear to be economically favorable in comparison to the conventional process. The fixed capital for the proposed di-calcium phosphate process is about 13 percent greater than a conventional normal superphosphate plant, but the manufacturing cost and the working capital are lower.

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# APPENDIX

A solution contains 47.10 percent $P_2O_5$, 5.50 percent CaO, 0.51 percent $SO_3$ and 46.89 percent $H_2O$.

Basis = 100 grams of solution:

$$\text{gram moles of } (PO_4)_2 = \frac{47.10}{142} = 0.332$$

$$\text{gram moles of } Ca_3 = \frac{5.50}{(56)(3)} = 0.0327$$

$$\text{gram moles of } (SO_3)_3 = \frac{0.51}{(80)(3)} = 0.00213$$

$$\text{gram moles of } H_2O = \frac{46.89}{18} = 2.61$$

Because the total gram moles of $(PO_4)_2$ and $(SO_3)_3$ must equal the total gram moles of $Ca_3$ and $H_6$, the number of moles of $H_6$ will be $0.332 + 0.00213 - 0.0327 = 0.30143$.

Hence the values of X and Y are:

$$X = \frac{(PO_4)_2}{(PO_4)_2 + (SO_3)_3} = \frac{0.332}{0.332 + 0.00213} = 0.994$$

$$Y = \frac{H_6}{H_6 + Ca_3} = \frac{0.30143}{0.0327 + 0.30143} = 0.902$$

The free water in the solution is $2.61 - 0.9043 = 1.7057$ moles. Hence, the "free water" present for 2 gram moles in total is:

$$m = \frac{1.7057}{0.33413} = 5.11$$

The solution is therefore represented by:

$$X = 99.4, \quad Y = 90.2, \quad m = 5.11$$